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THESE

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à l'UNIVERSITE DE PROVENCE

pour obtenir

LE GRADE DE DOCTEUR ES-SCIENCES PHYSIQUES

par

Madame FOURNIER Josette
Ancienne élève de l'Ecole Normale Supérieure
de l'Enseignement Technique
Agrégée de l'Université
Docteur de spécialité

* * *

CALCULS DE CONFORMATIONS SUR DES SYSTEMES TENDUS : TETRAMETHYL-1,1,3,3 CYCLOHEXANE, BICYCLO [3.1.1] HEPTANE, BICYCLO [3.2.1] OCTANE. EFFET REFLEXE

Soutenue le 17 Juin 1972 devant la Commission d'Examen.

MM. J.	METZGER	*Président*
P.	MAITTE	*Examinateurs*
J.C.	MAIRE	
B.	WAEGELL	
E.J.	VINCENT	
J.M.	LEHN	*Rapporteur extérieur*

ANNEXE.I

FIGURES :

Le nombre porté sous chaque figure représente l'énergie de contrainte totale, ΣW.
Pour les dérivés bromés, le second nombre représente la différence entre ΣW et l'énergie attractive Br...H.

1 cm représente 1 Å

La discussion de [illegible] résultats se trouve dans la partie principale [illegible] (p. ...). Les résultats numériques sont rassemblés dans l'annexe II (p. ...).

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ANNEXE B

FIGURES :

Le nombre porté sous chaque figure représente l'énergie de contrainte totale, ΣW.

Pour les dérivés bromés, le second nombre représente la différence entre ΣW et l'énergie attractive Br...H.

2 cm représentent 1 Å

La discussion de ces résultats se trouve dans la partie principale de la thèse (*), les résultats numériques correspondants sont dans l'annexe A (**).

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.../...

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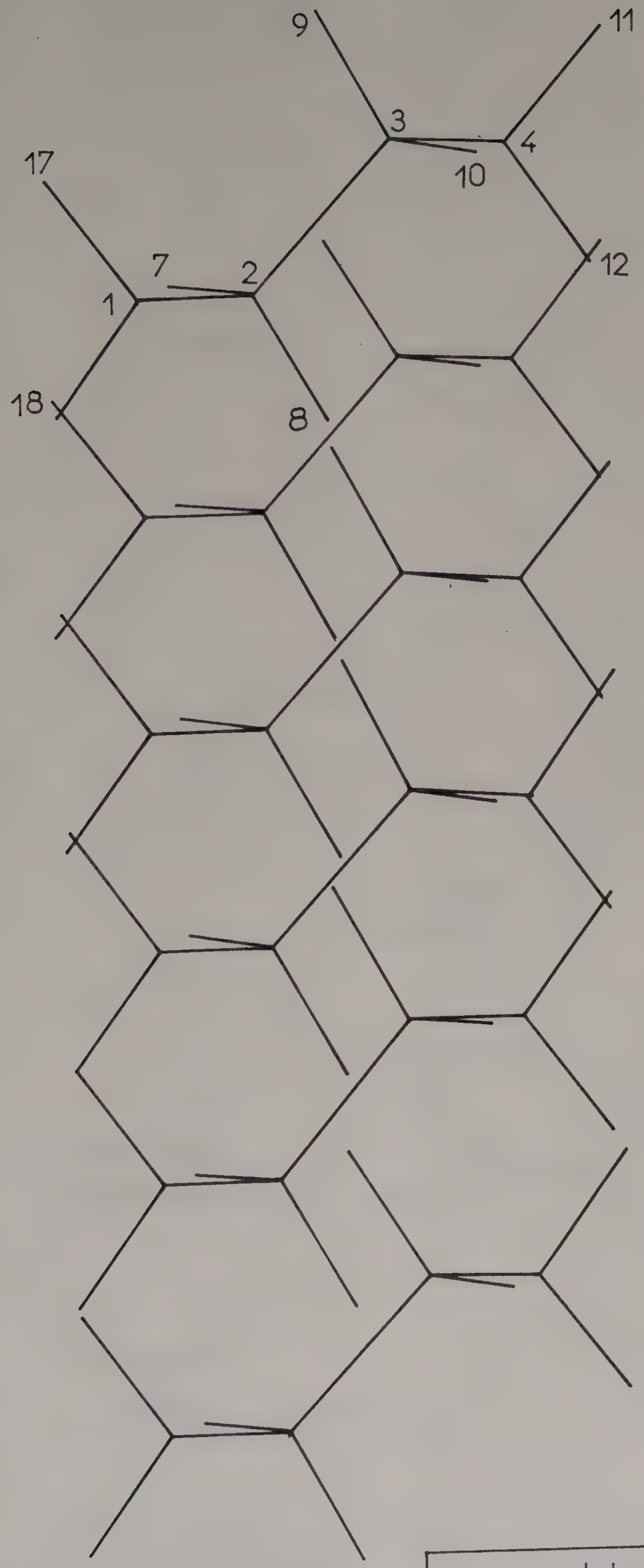


Figure 1

30 variables -4,708 kcal.

Figure 2

30 variables 1,522 kcal

Figure 3

30 variables -5,782 kcal

Figure 4

30 variables 1,603 kcal

Figure 5

12 variables 1,464 kcal

Figure 6

12 variables - 1,455 kcal

cyclohexane

conformation chaise

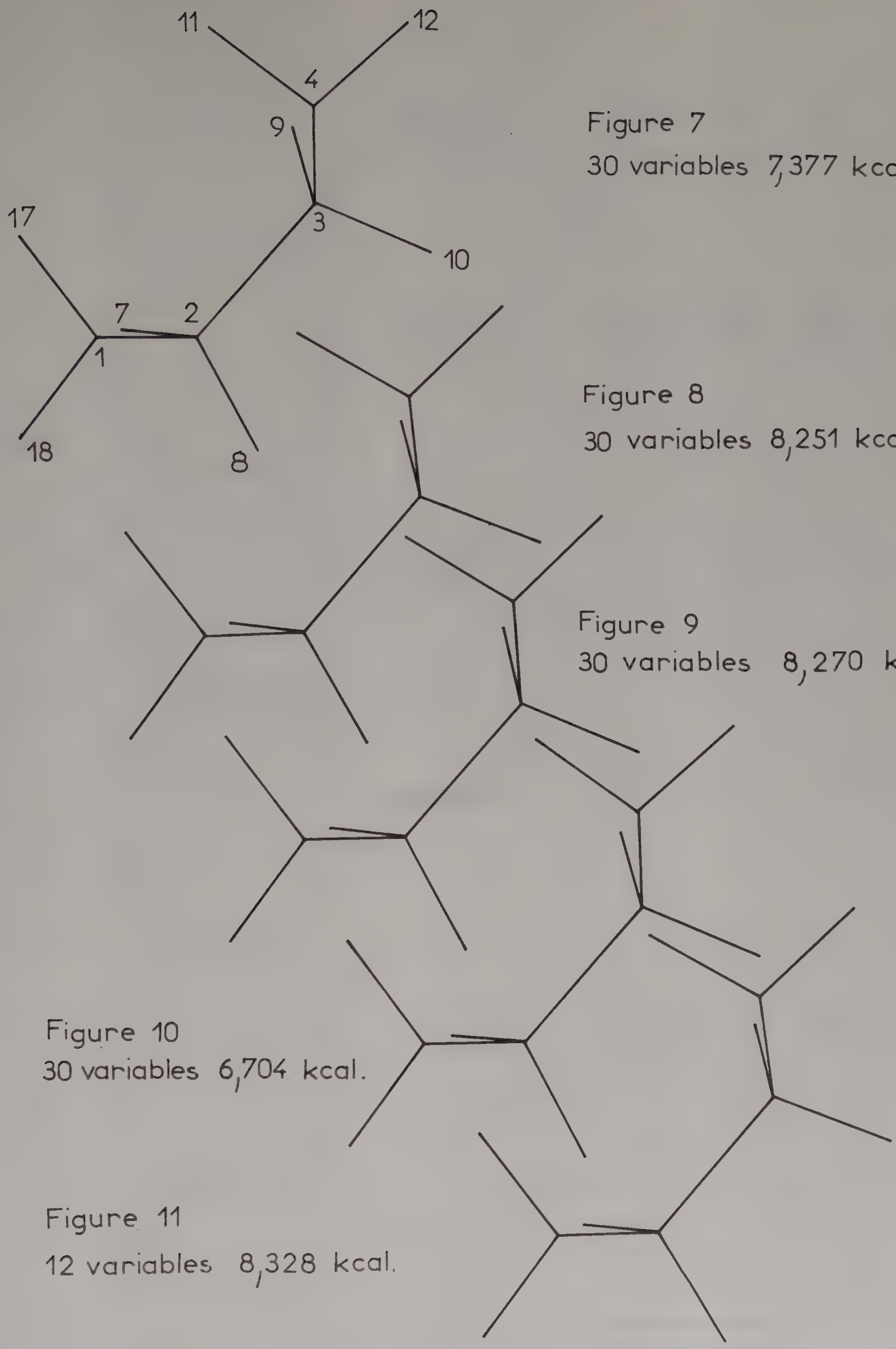


Figure 7
30 variables 7,377 kcal.

Figure 8
30 variables 8,251 kcal.

Figure 9
30 variables 8,270 kcal.

Figure 10
30 variables 6,704 kcal.

Figure 11
12 variables 8,328 kcal.

cyclohexane
conformation bateau

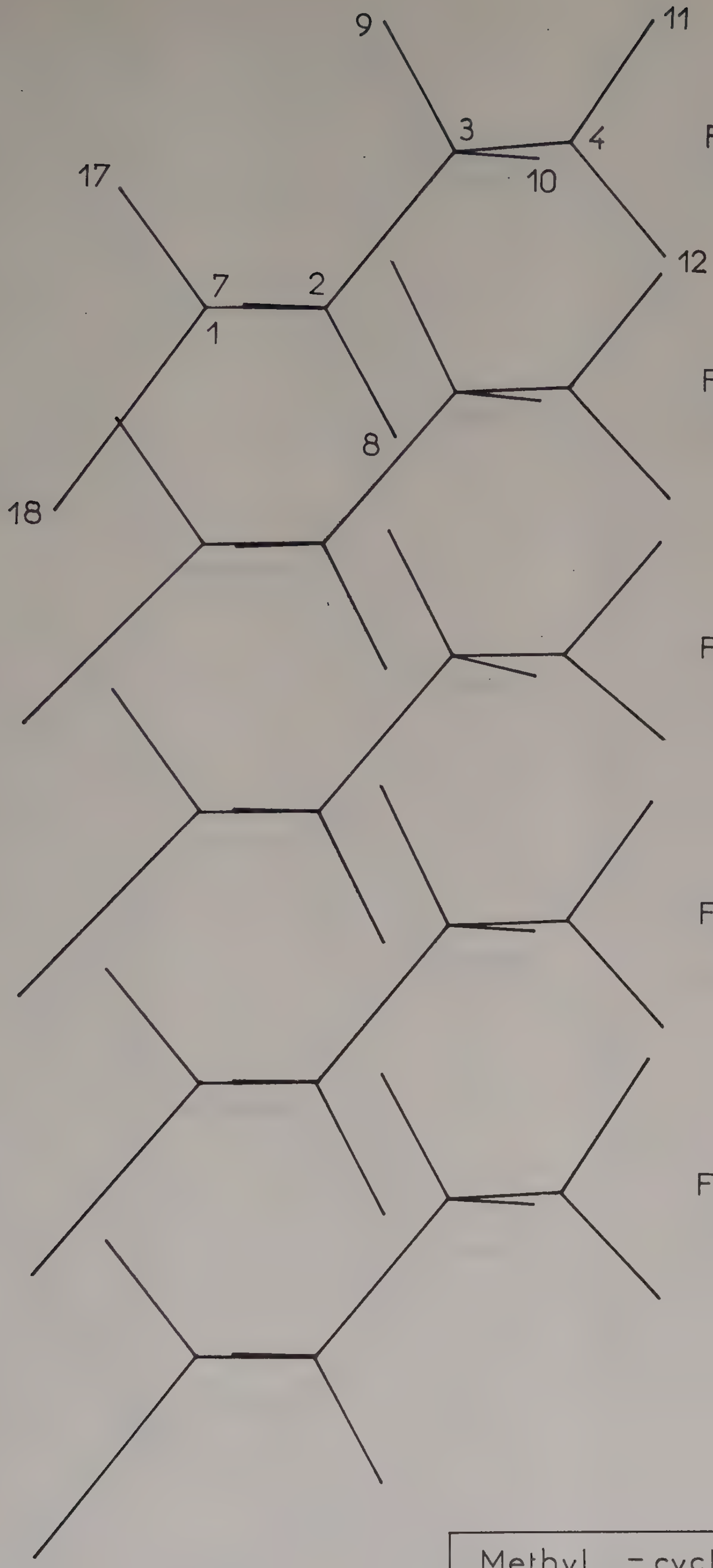


Figure 12 11,211 kcal.

Figure 13 2,291 kcal.

Figure 14 1,822 kcal.

Figure 15 - 0,297 kcal.

Figure 16 0,152 kcal.

Methyl $_{eq}$ - cyclohexane
12 variables

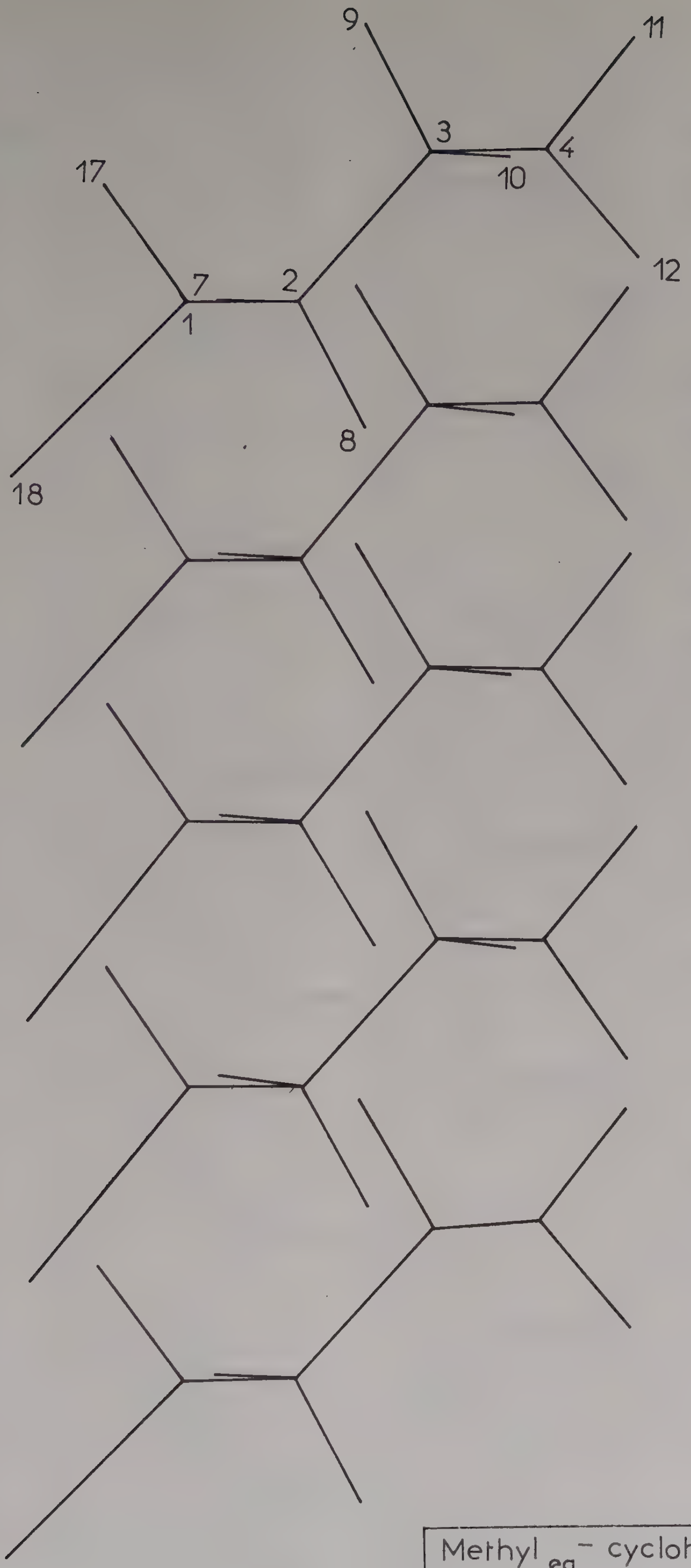


Figure 17
12 variables 2,330 kcal

Figure 18
12 variables 4,532 kcal.

Figure 20
30 variables 4,651 kcal.

Figure 21
30 variables 4,703 kcal.

Figure 19
12 variables 2,327 kcal.

Methyl_{eq} – cyclohexane

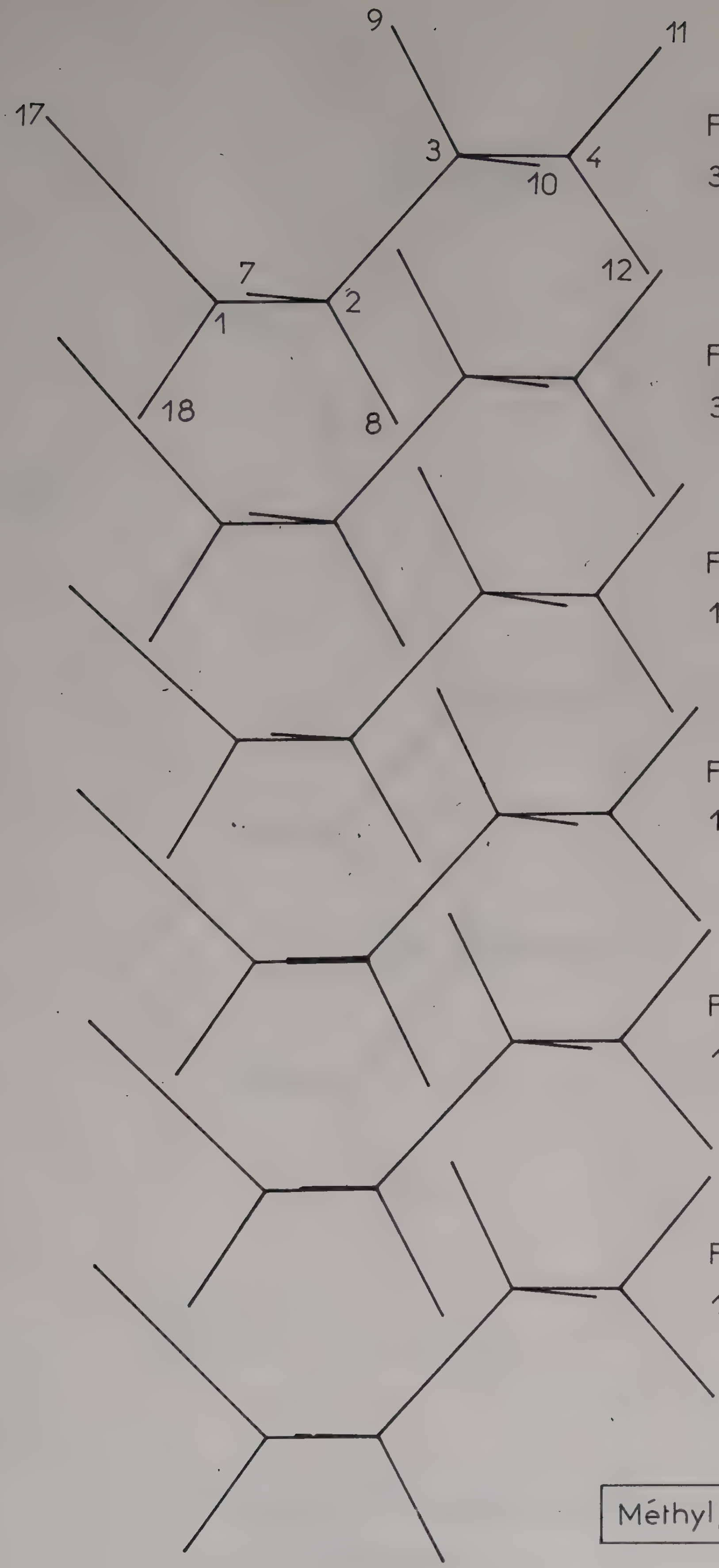


Figure 22
30 variables 6,476 kcal.

Figure 23
30 variables 6,639 kcal.

Figure 24
12 variables 6,302 kcal.

Figure 25
12 variables 2,924 kcal.

Figure 26
12 variables 3,850 kcal.

Figure 27
12 variables 2,181 kcal.

Méthyl$_{ax}$-cyclohexane

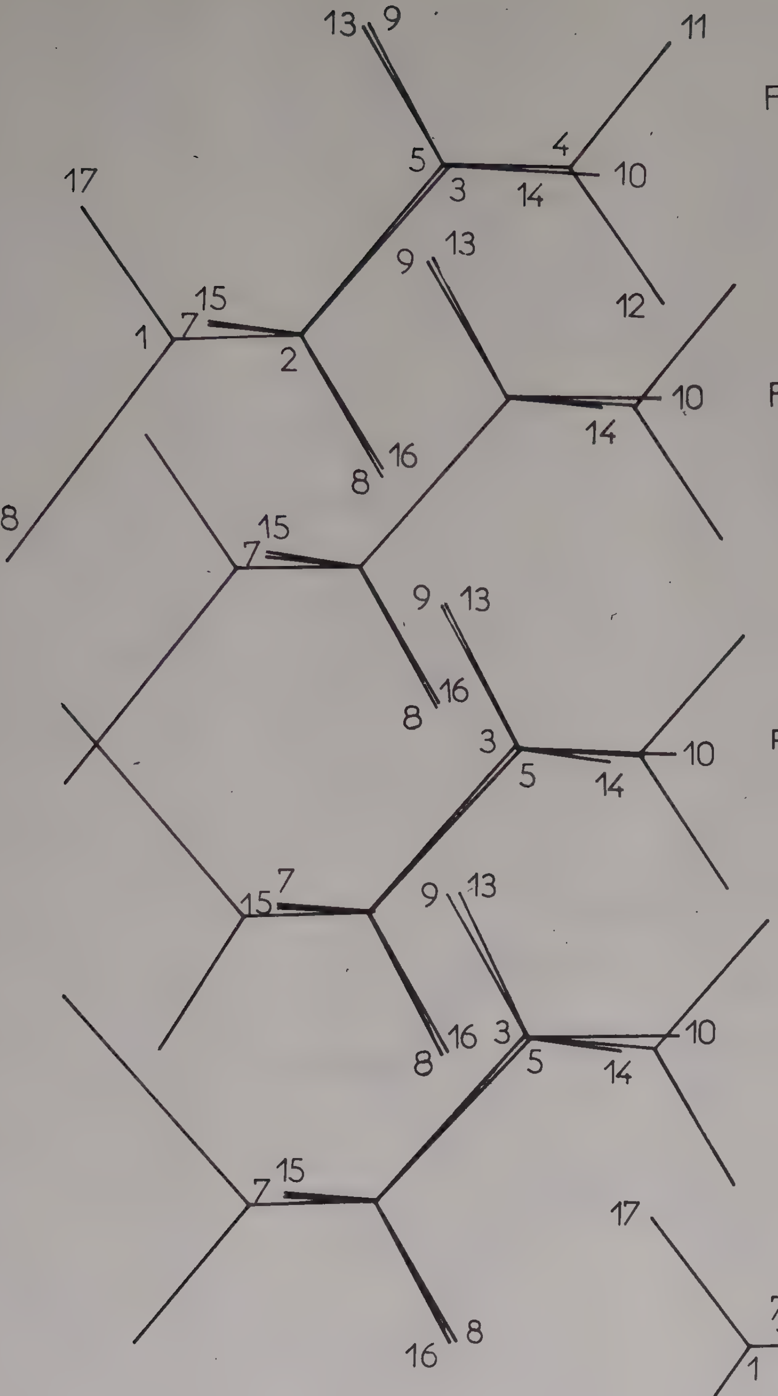


Figure 28
isomère cis 8,465 kcal.

Figure 29
isomère cis 8,148 kcal.

Figure 30
isomère trans 10,372 kcal.

Figure 31
isomère trans 10,118 kcal.

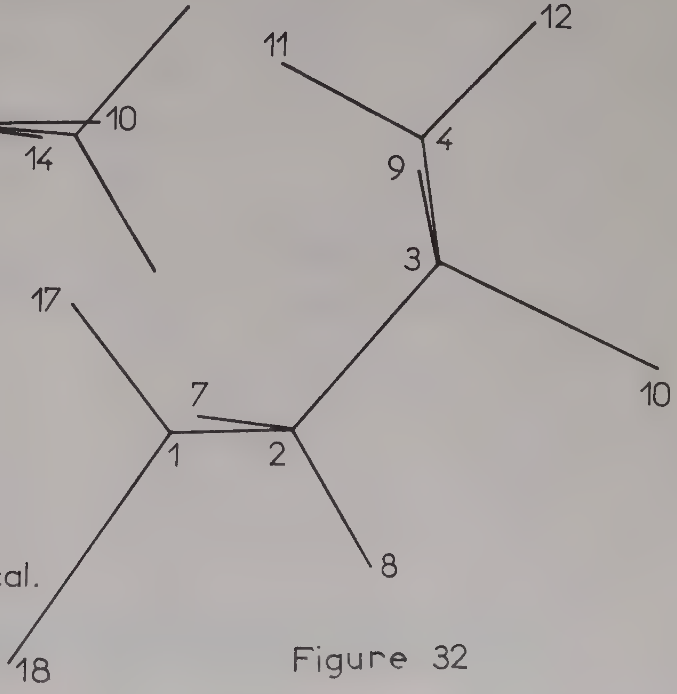


Figure 32
isomère cis 19,969 kcal.
conformation bateau

dimethyl – 1,3 cyclohexane
30 variables

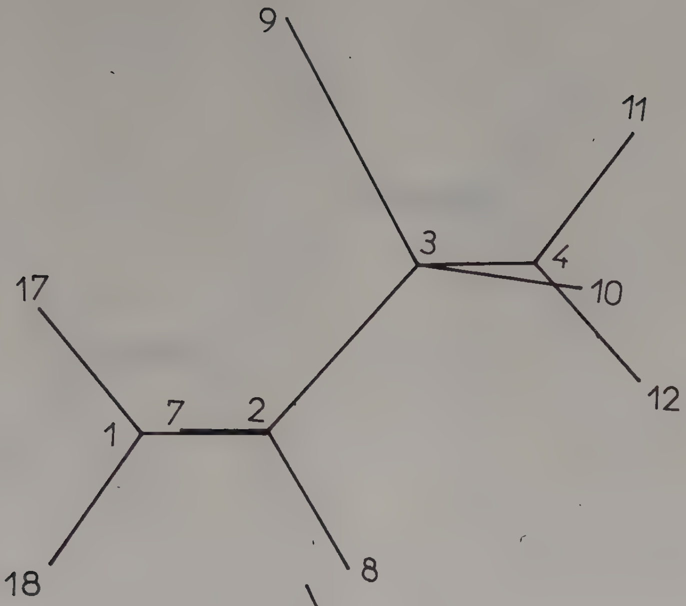


Figure 33
26,695 kcal.

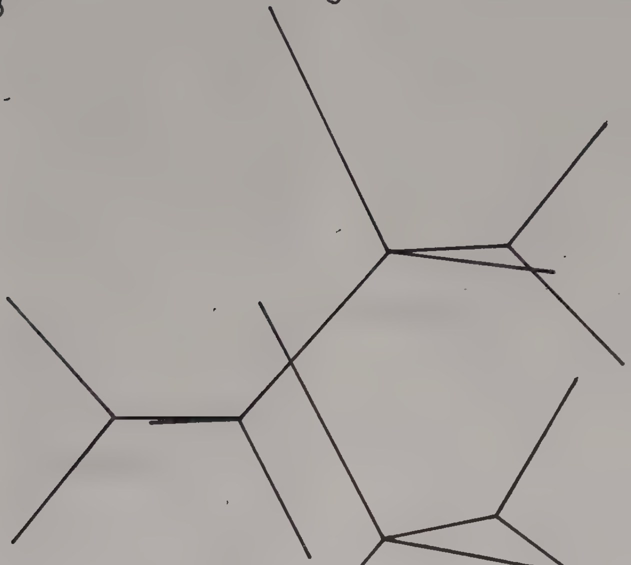


Figure 34
21,242 kcal.

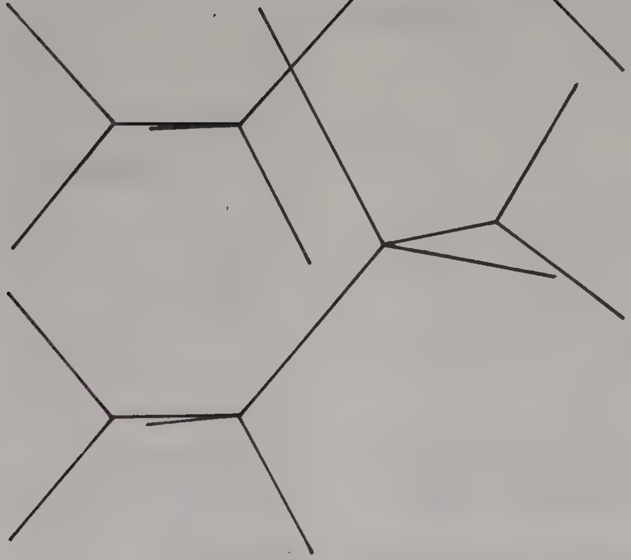
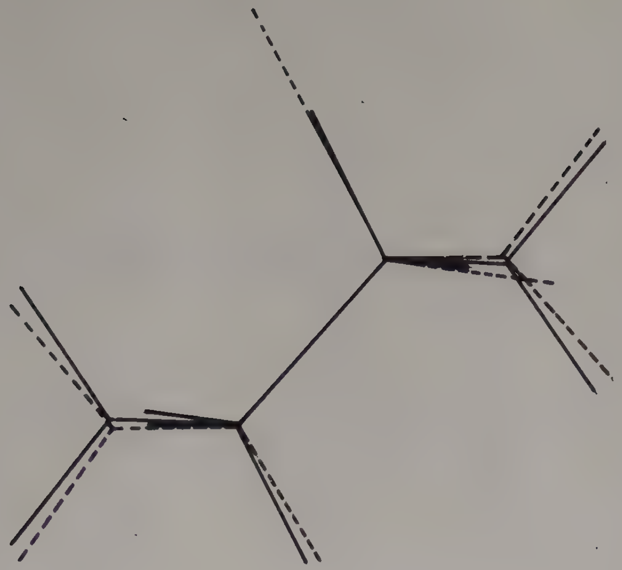
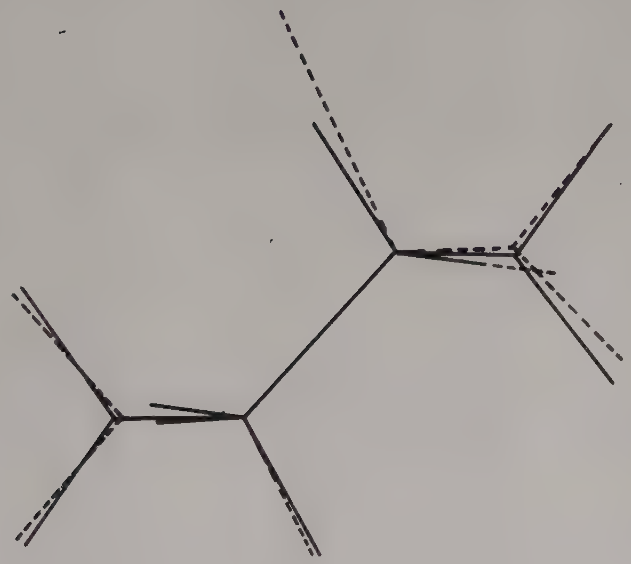


Figure 35
6,905 kcal.

tétraméthyl-1,1,3,3 cyclohexane
12 variables



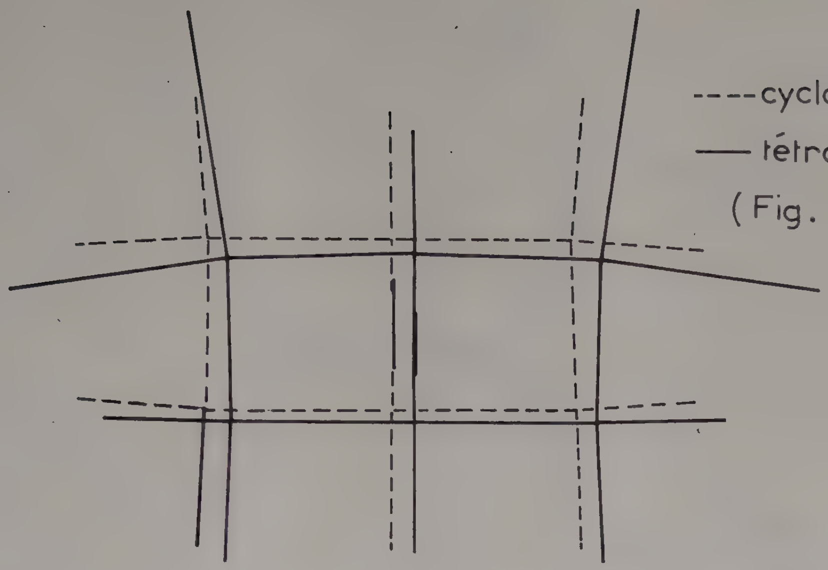
tétraméthyl - 1,1,3,3 cyclohexane
et cyclohexane (Fig. 5 - Fig 33)



tétraméthyl - 1,1,3,3 cyclohexane
et cyclohexane (Fig. 6 - Fig 34)

Figure 36

superposition dans le plan y-z
de projections du cyclohexane
et tétraméthyl - 1,1,3,3 cyclohexane

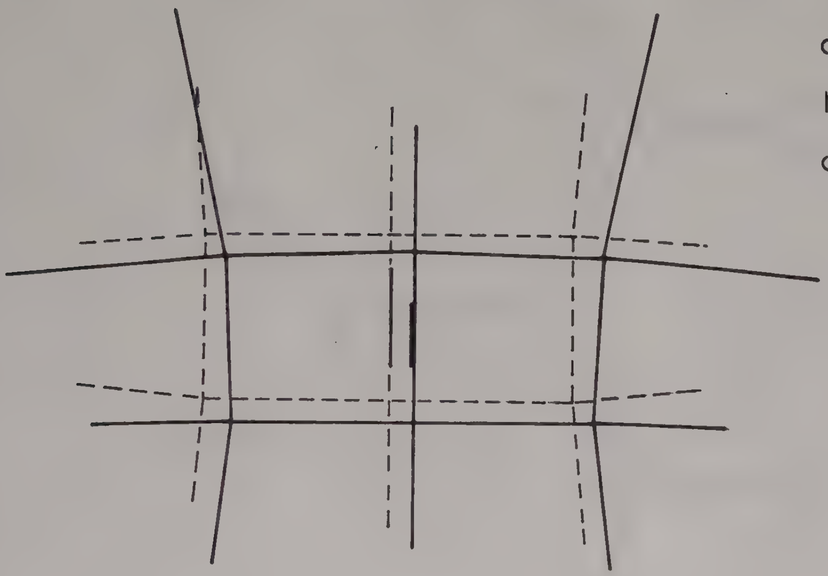


----cyclohexane (Fig.5)

—— tétraméthyl-1,1,3,3 cyclohexane (Fig. 33)

Figure 37

superposition dans le plan x-z
de projections du cyclohexane
et tétraméthyl-1,1,3,3 cyclohexane



cyclohexane (Fig.6)

tétraméthyl-1,1,3,3 cyclohexane (Fig.34)

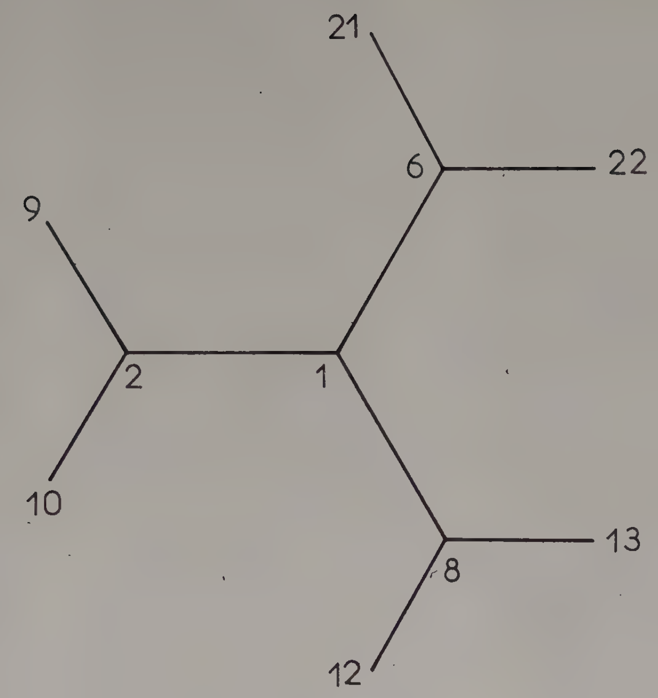


Figure 38
3 variables 11,789 kcal.

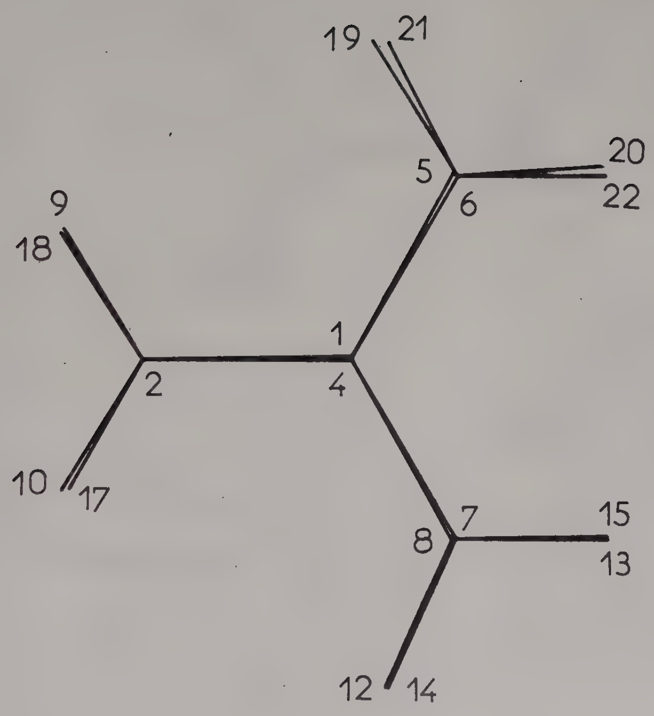


Figure 39
37 variables 11,715 kcal.

bicyclo [2,2,2] octane

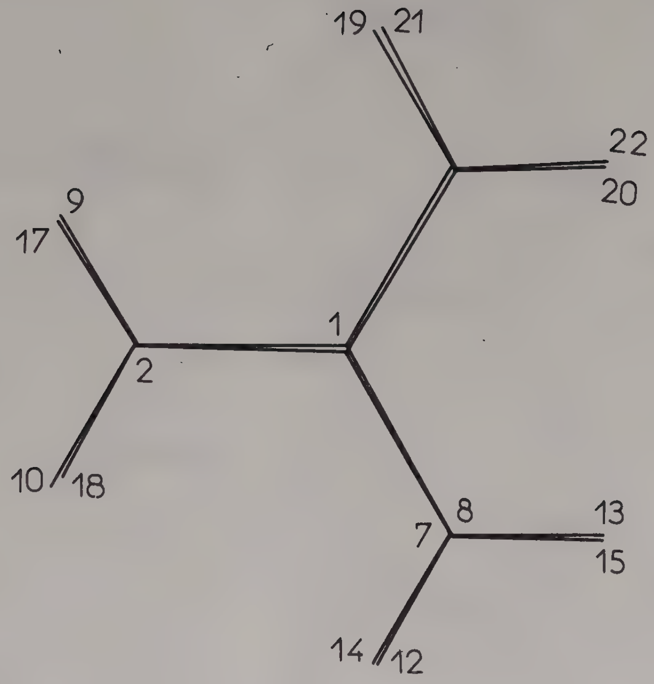


Figure 40

8 variables 11,546 kcal.

bicyclo [2,2,2] octane

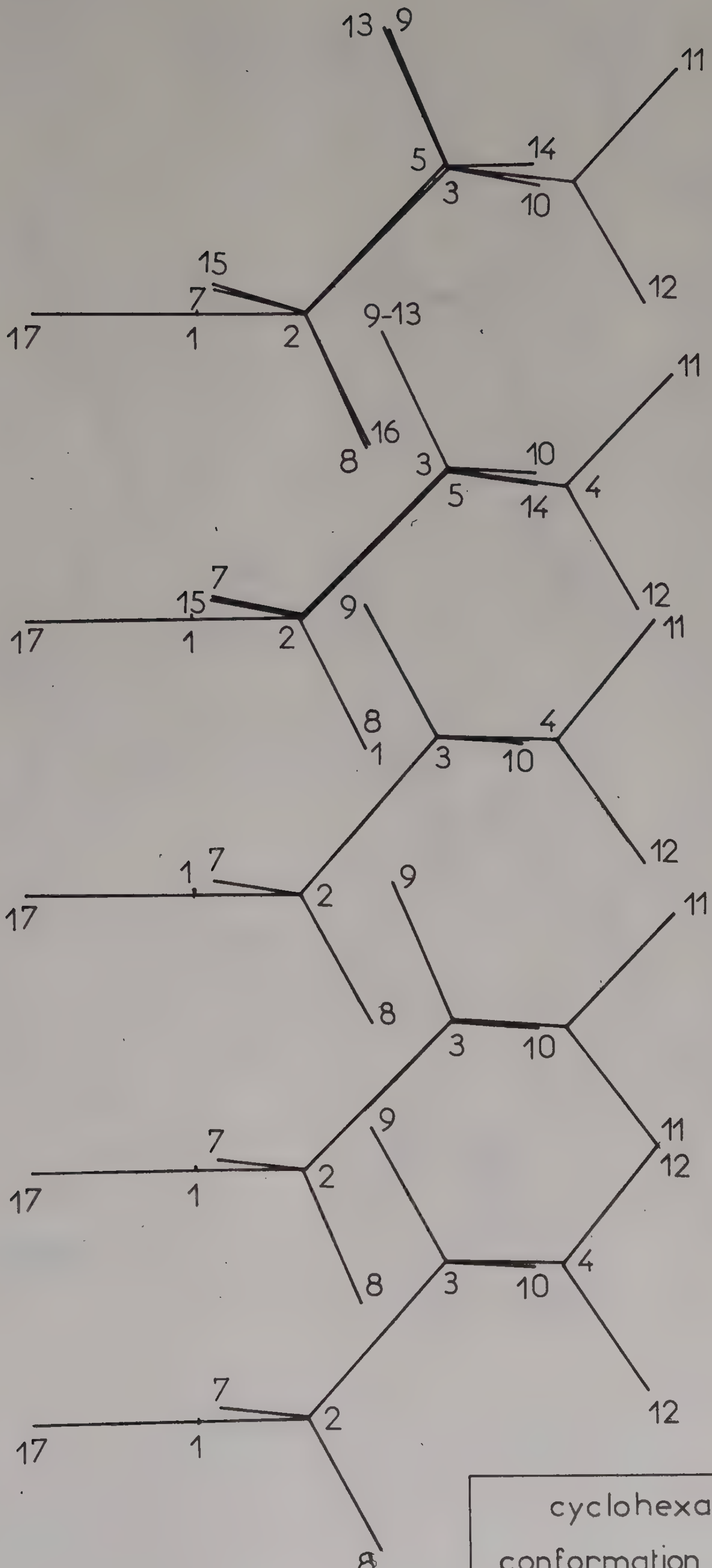


Figure 41
1,487 kcal.

Figure 42
-3,670 kcal.

Figure 43
0,943 kcal.

Figure 44
-0,026 kcal.

Figure 45
-3,083 kcal.

cyclohexanone
conformation chaise

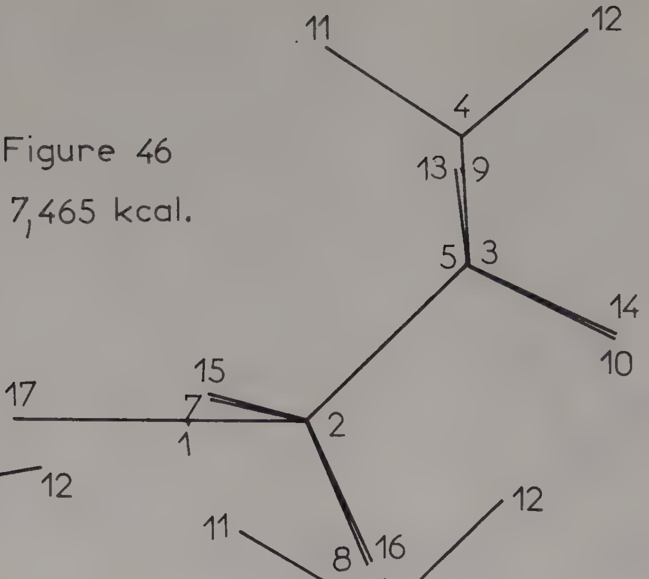


Figure 46

7,465 kcal.

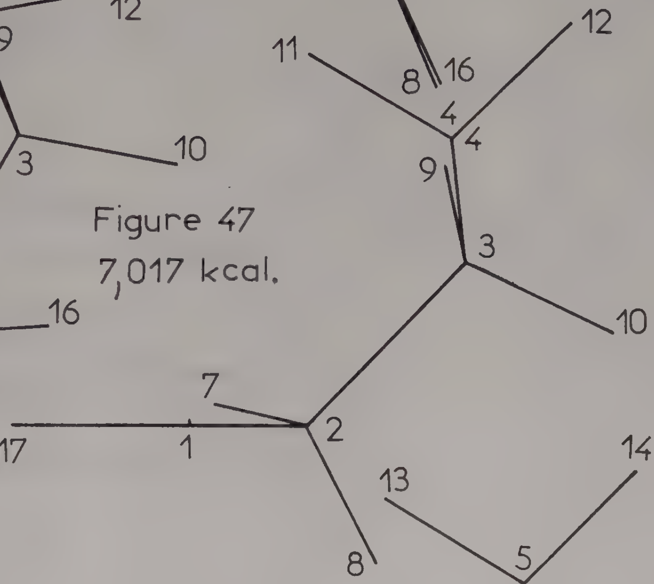


Figure 47

7,017 kcal.

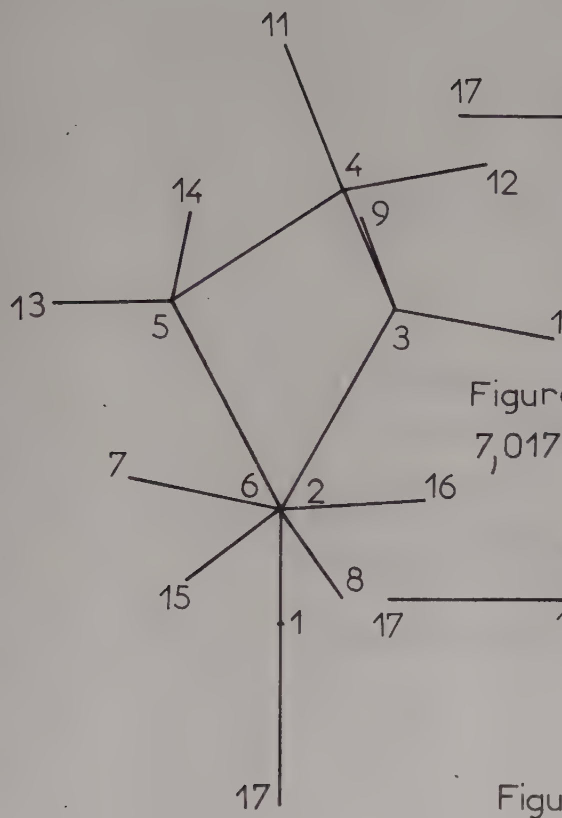


Figure 49

6,162 kcal.

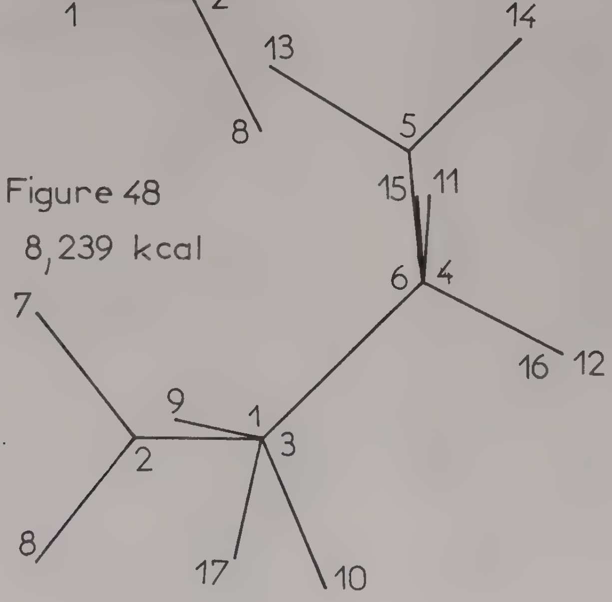


Figure 48

8,239 kcal

cyclohexanone
conformation
"bateau déformé"

Figure 50

13,017 kcal.

14,159 kcal

FIGURE 50 BIS

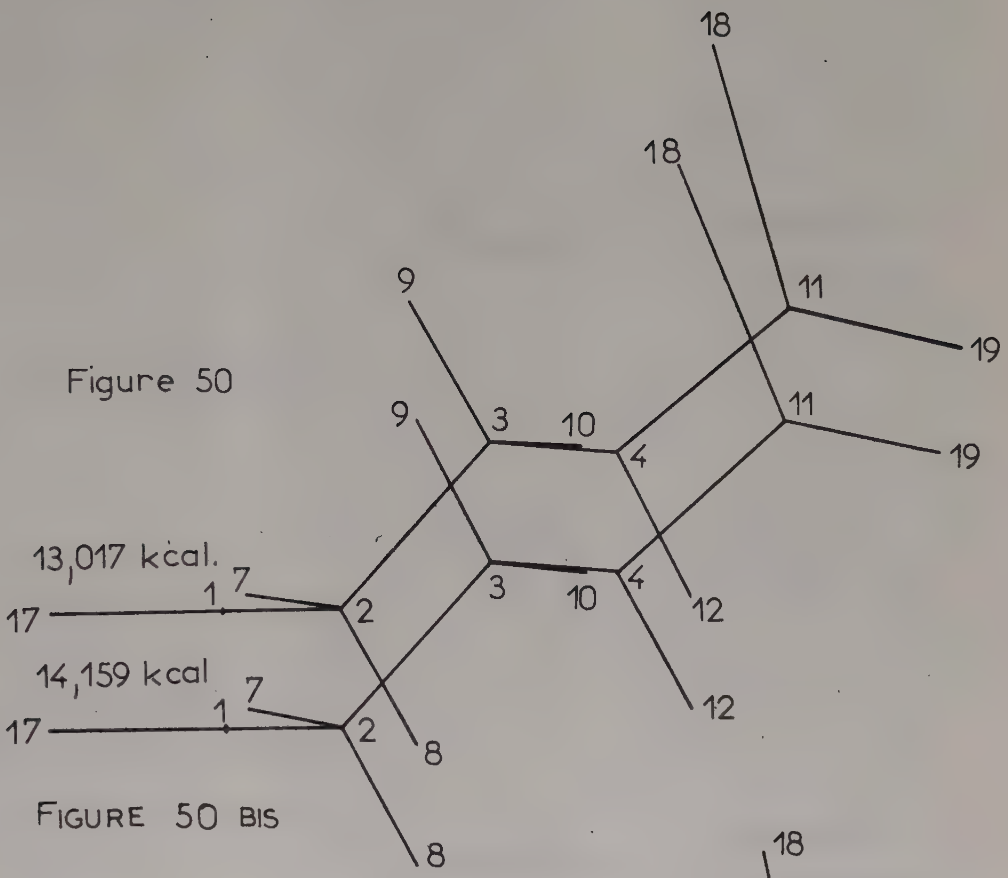
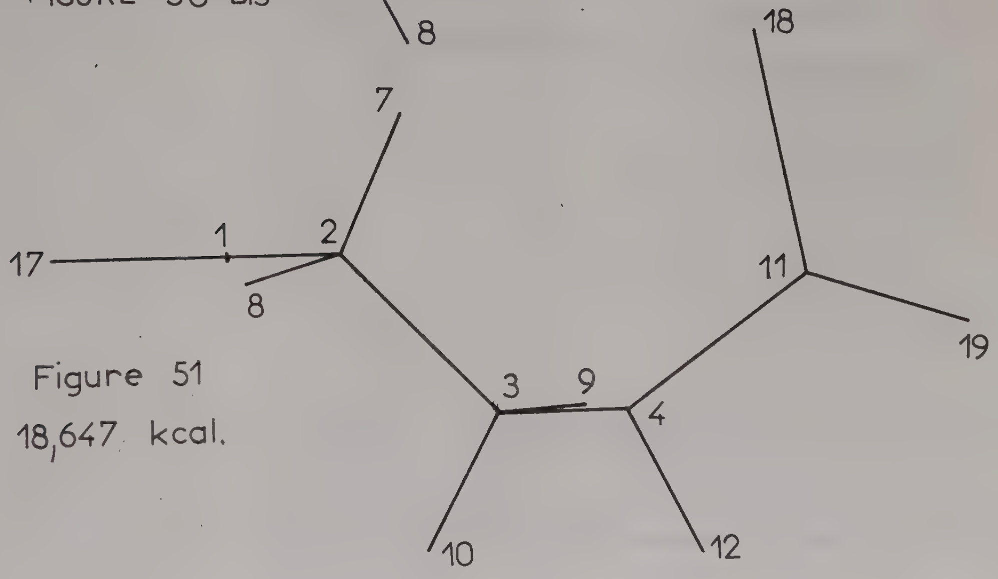


Figure 51

18,647 kcal.



tertiobutyl-4 cyclohexanone

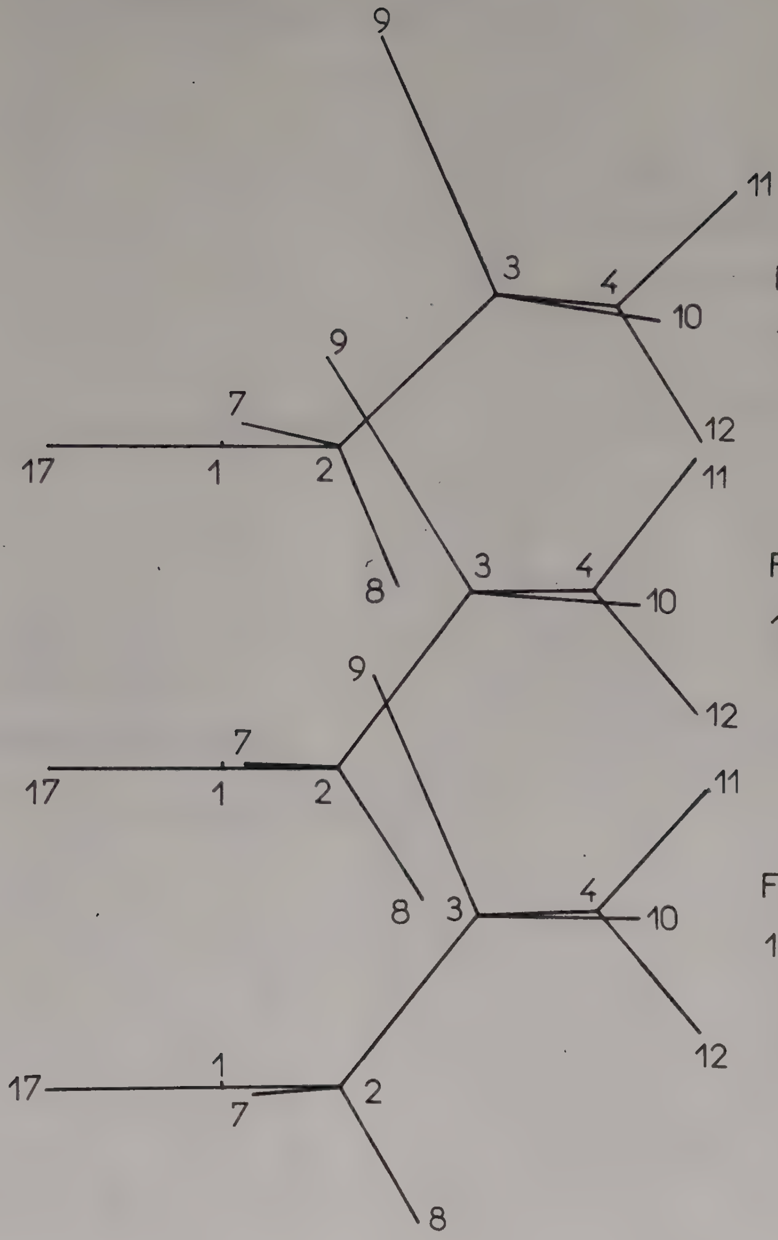


Figure 52
19,294 kcal.

Figure 53
18,586 kcal.

Figure 54
17,724 kcal.

tétraméthyl - 3,3,5,5 cyclohexanone
conformation chaise

tétraméthyl 3,3,5,5 cyclohexanone
conformations "bateau"

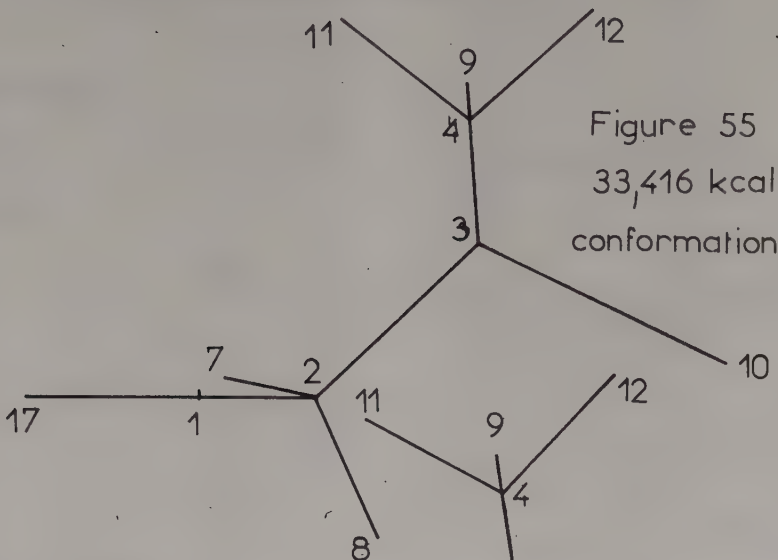


Figure 55
33,416 kcal.
conformation "bateau"

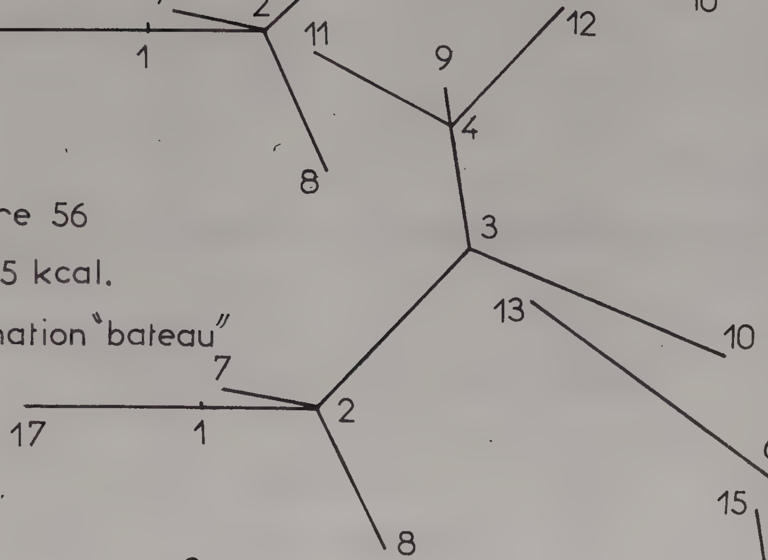


Figure 56
30,615 kcal.
conformation "bateau"

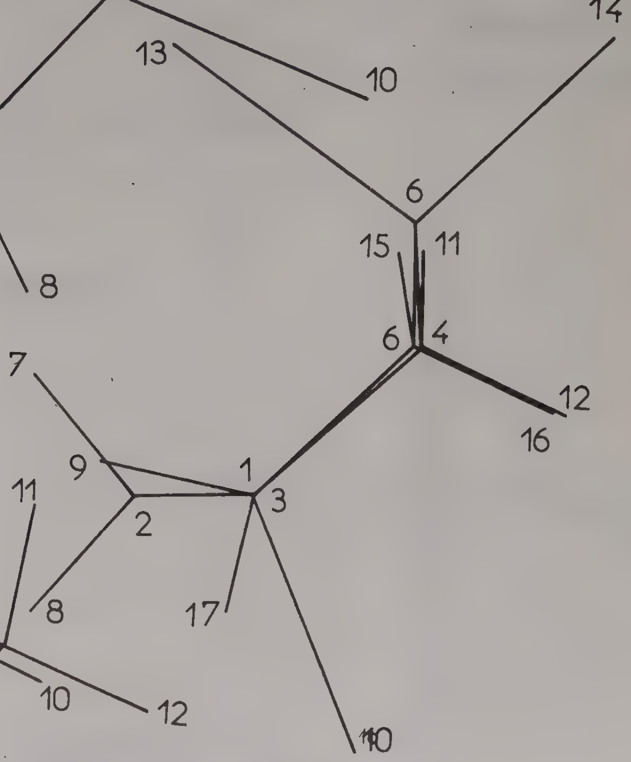


Figure 57
35,780 kcal.
conformation "bateau dissymètrique"

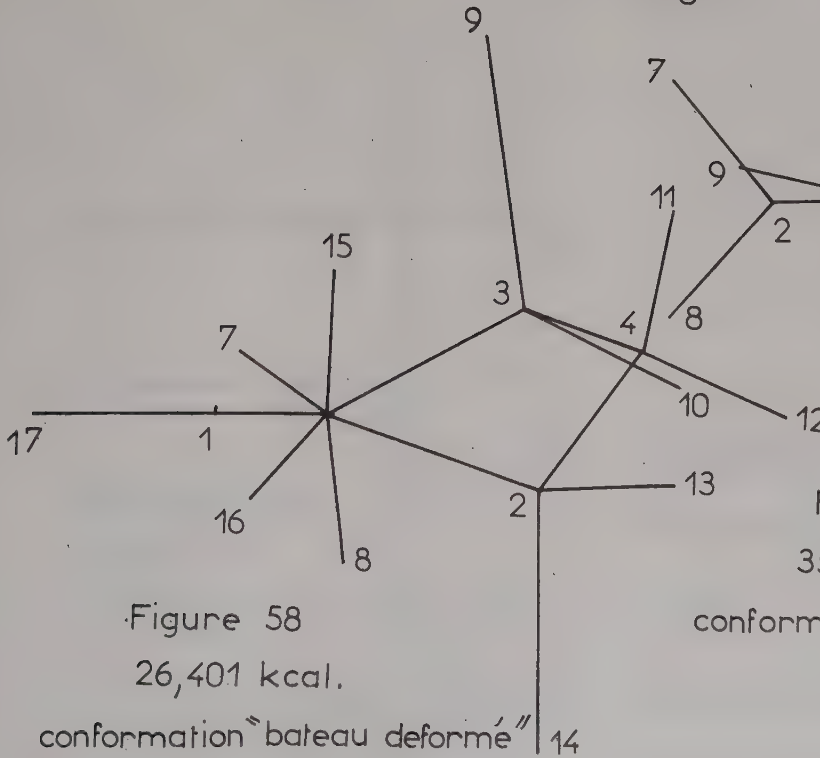


Figure 58
26,401 kcal.
conformation "bateau deformé"

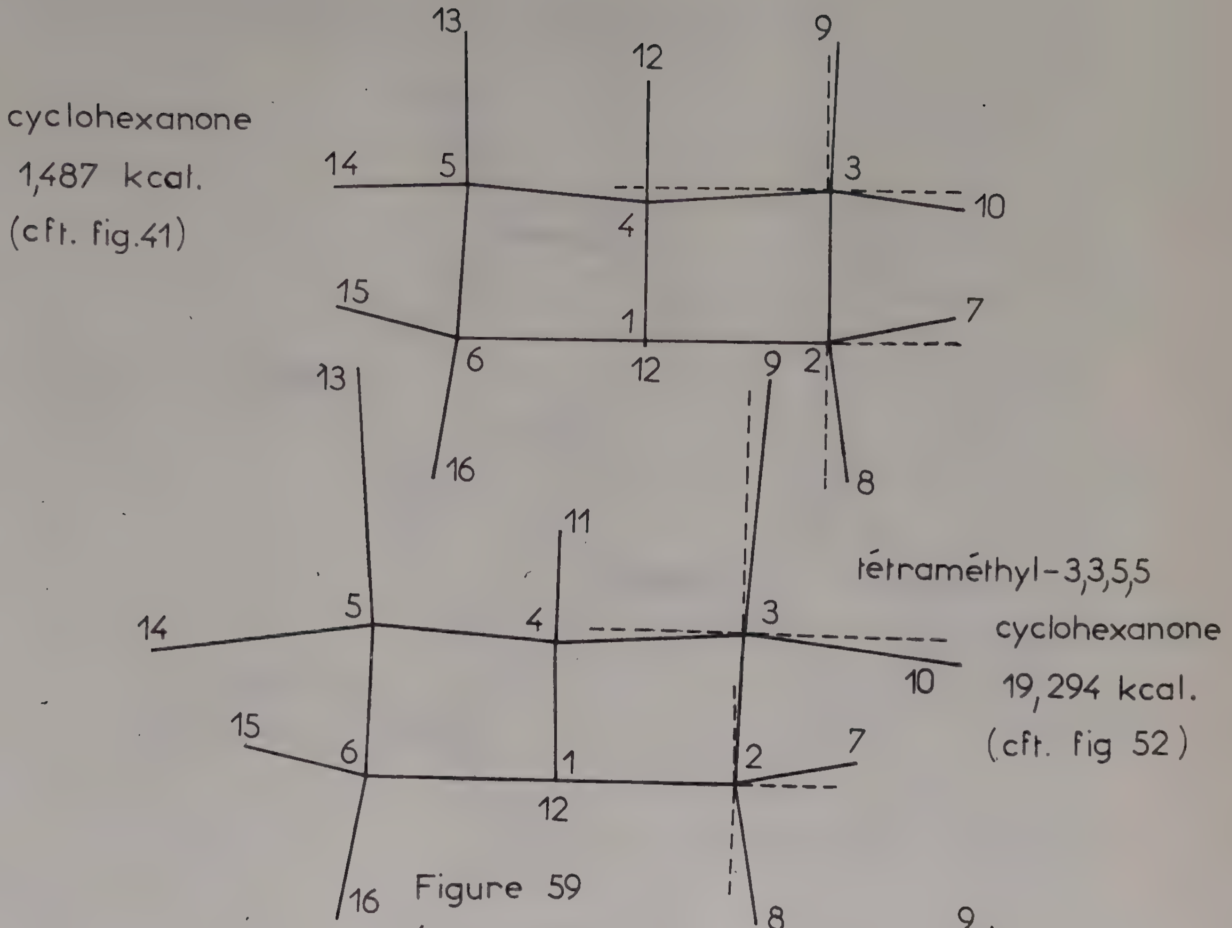


Figure 59

(27 variables)

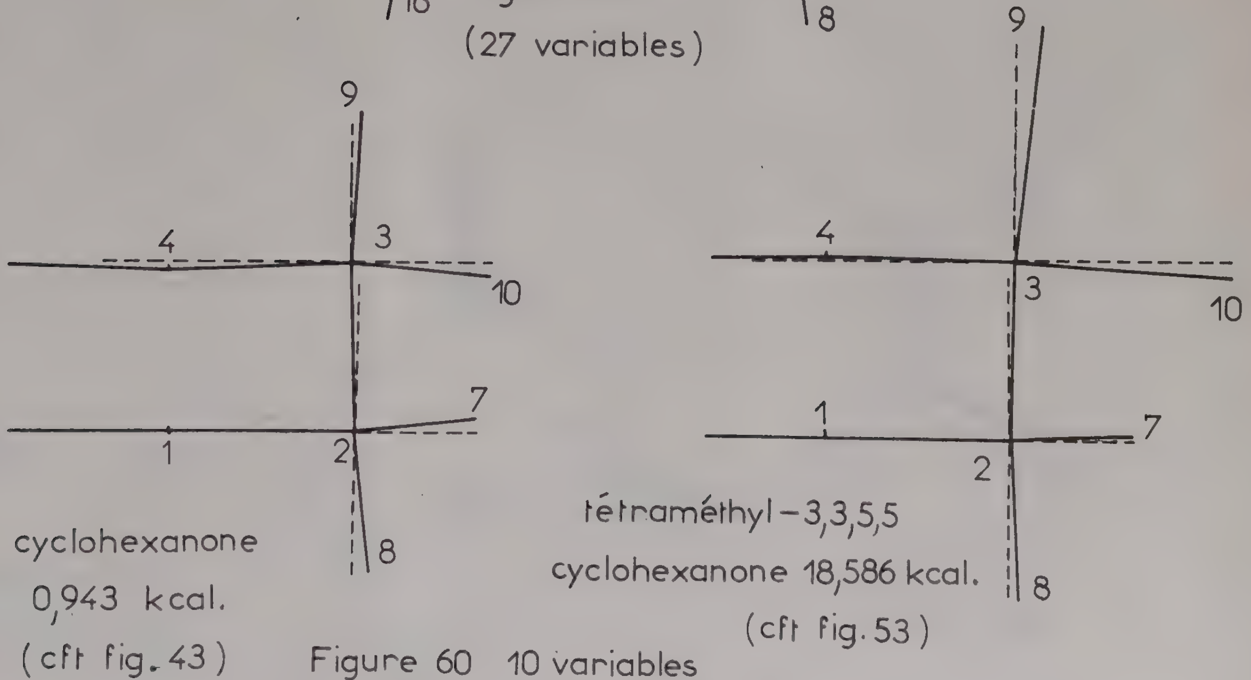


Figure 60 10 variables

projections dans le plan xz de la cyclohexanone et de la tétraméthyl-3,3,5,5 cyclohexanone

bromo-2 cyclohexanone

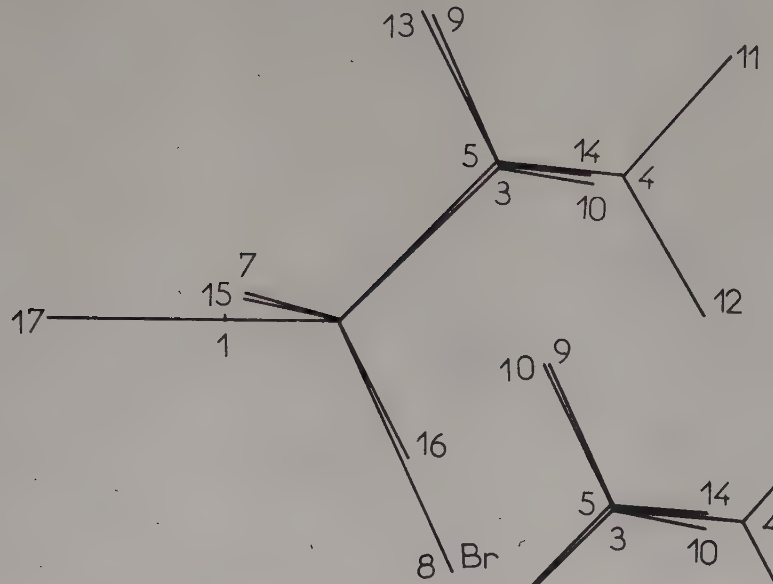


Figure 61
5,776 kcal.

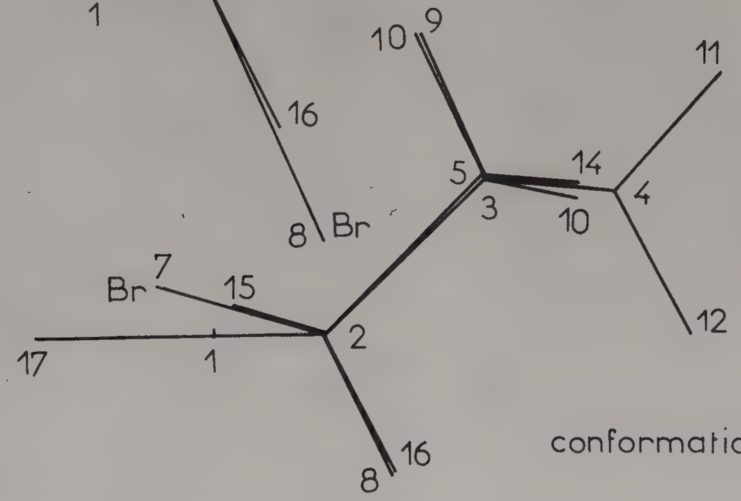
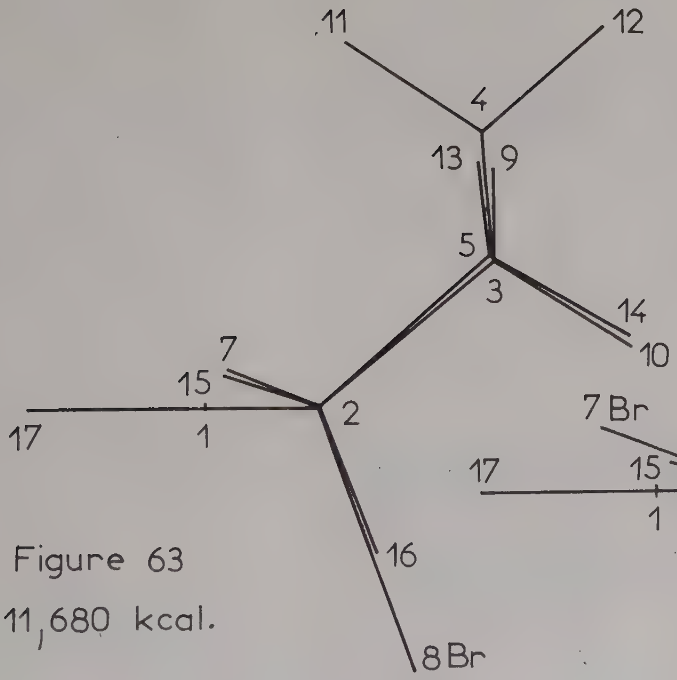


Figure 62
6,023 kcal.

conformations "chaise"



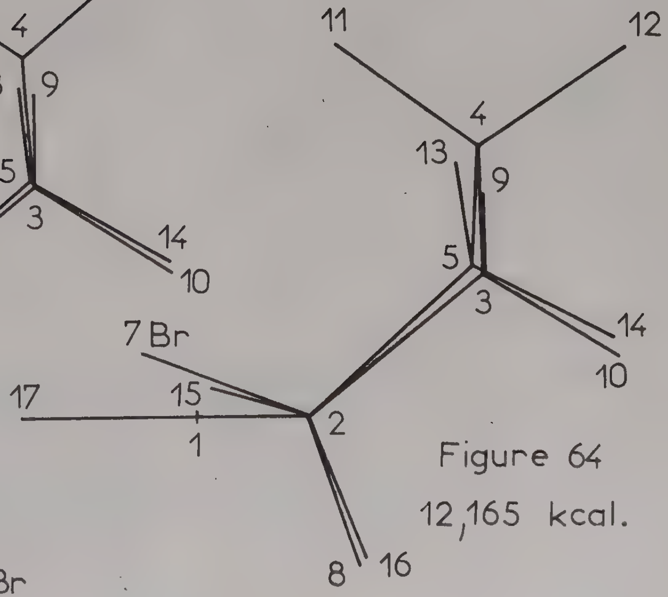


Figure 63
11,680 kcal.

Figure 64
12,165 kcal.

conformations "bateau"

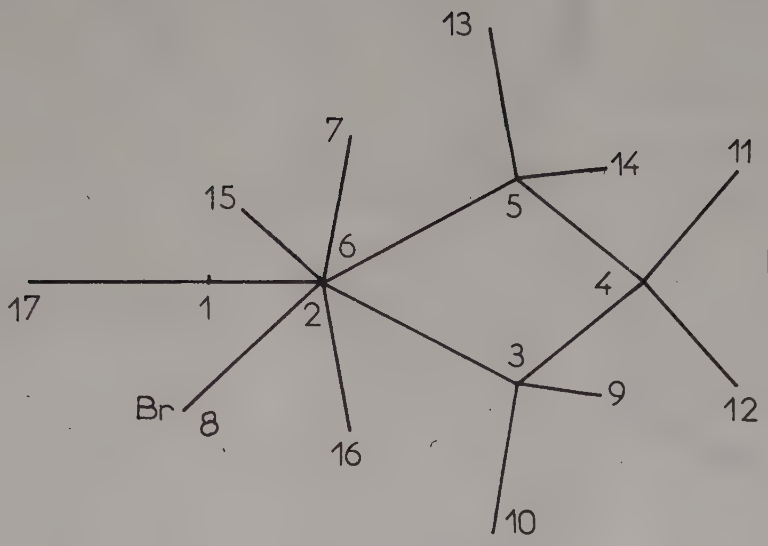


Figure 65
8,920 kcal.

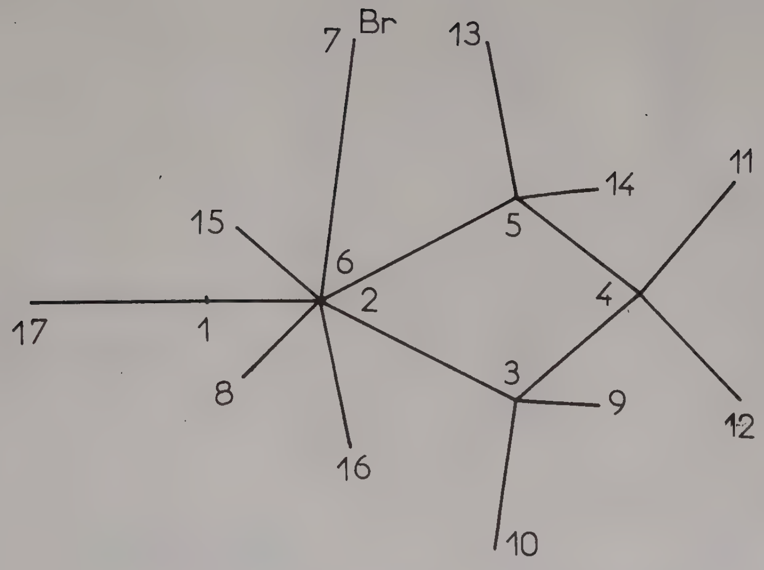


Figure 66
9,802 kcal

bromo-2 cyclohexanone
conformations "croisée"

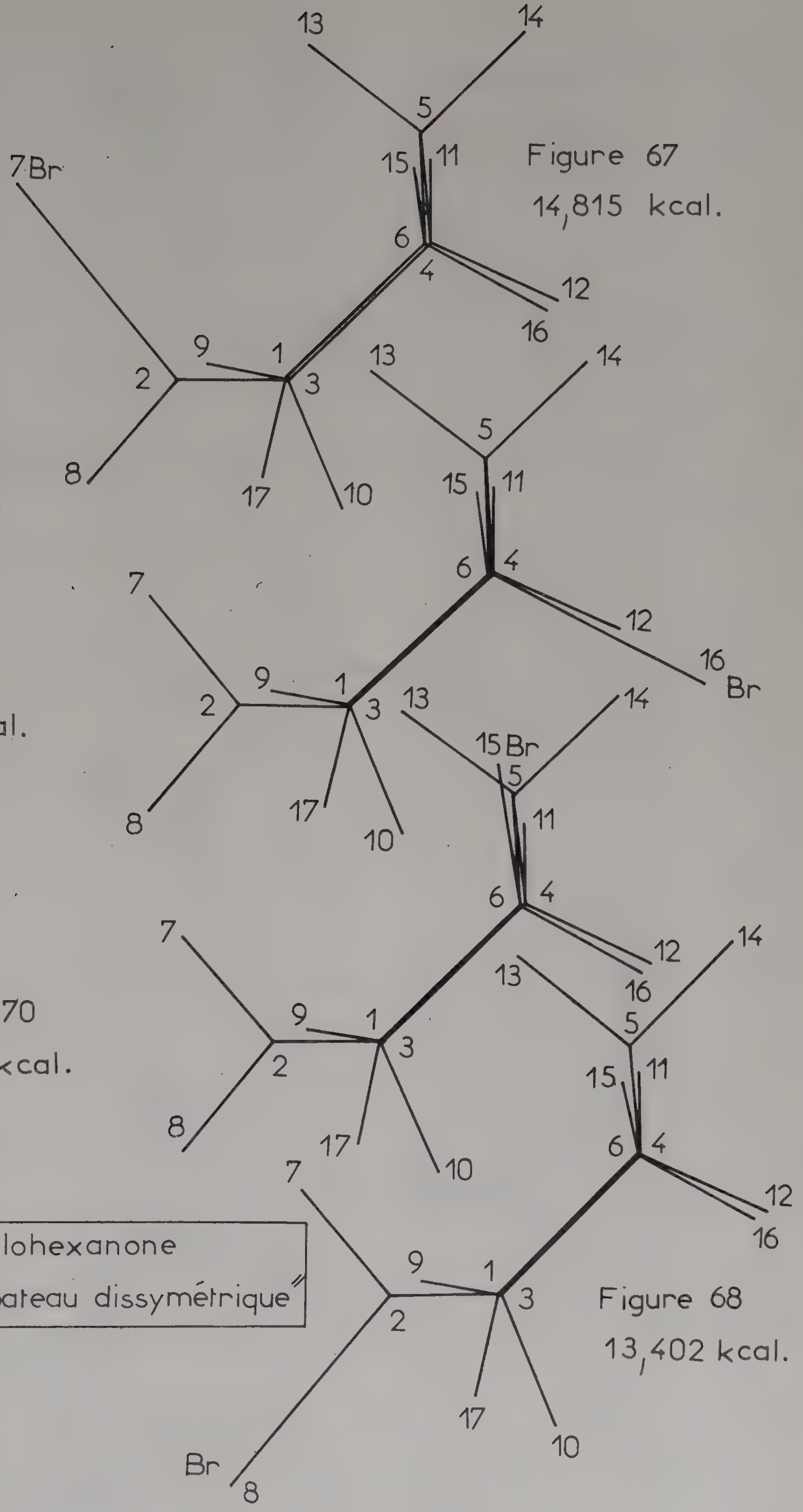


Figure 67
14,815 kcal.

Figure 69
14,082 kcal.

Figure 70
13,700 kcal.

Figure 68
13,402 kcal.

bromo-2 cyclohexanone
conformations "bateau dissymétrique"

bromo-2, tétraméthyl-3,3,5,5 cyclohexanone

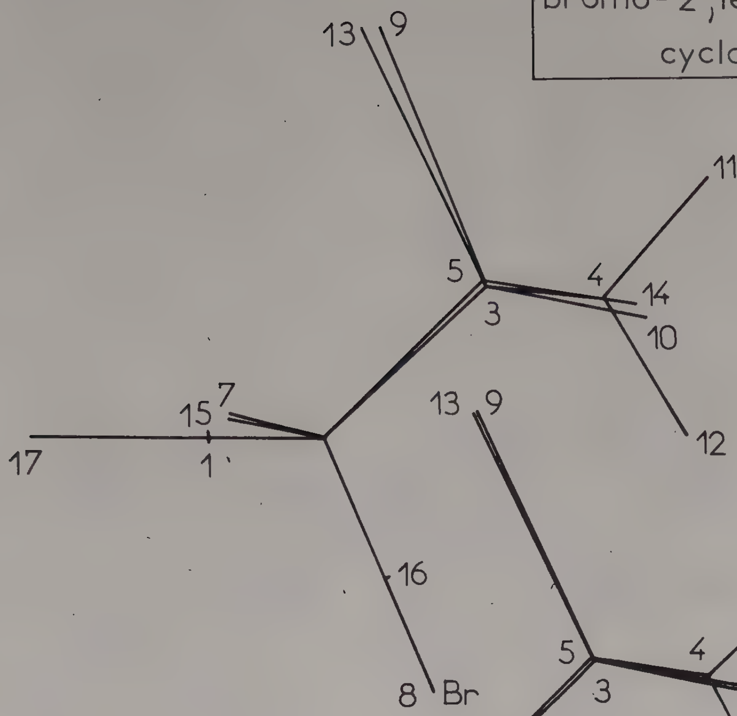


Figure 71
24,005 kcal.

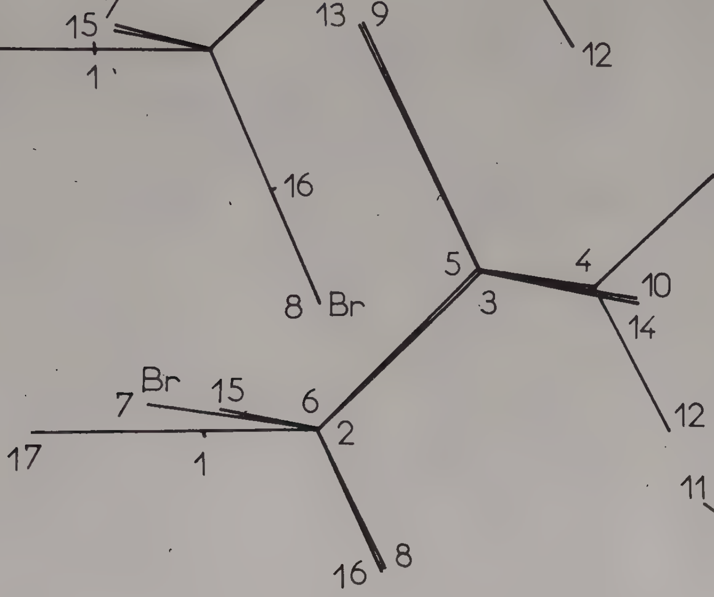


Figure 72
22,992 kcal.

conformations "chaise"

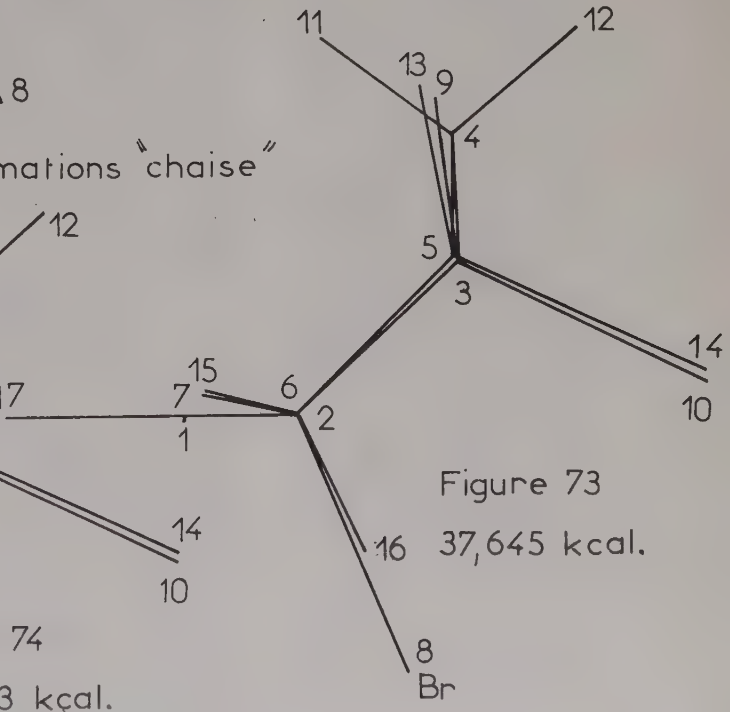


Figure 73
37,645 kcal.

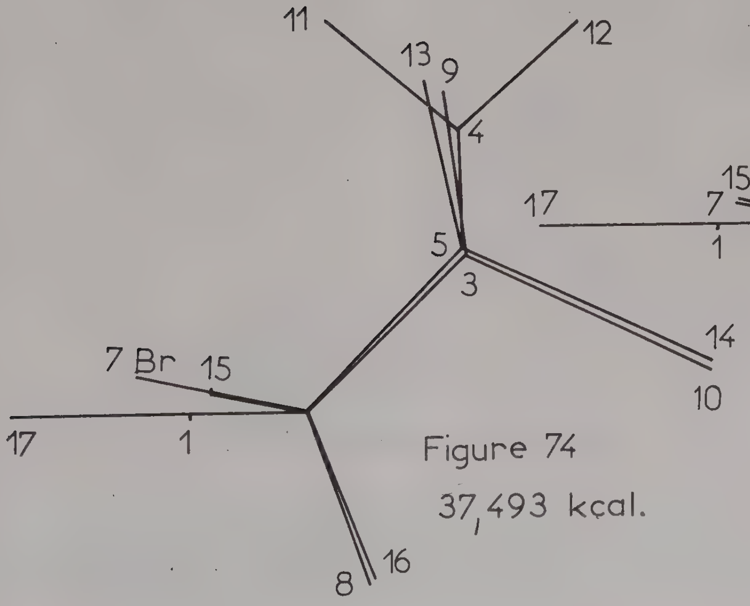


Figure 74
37,493 kcal.

conformations "bateau"

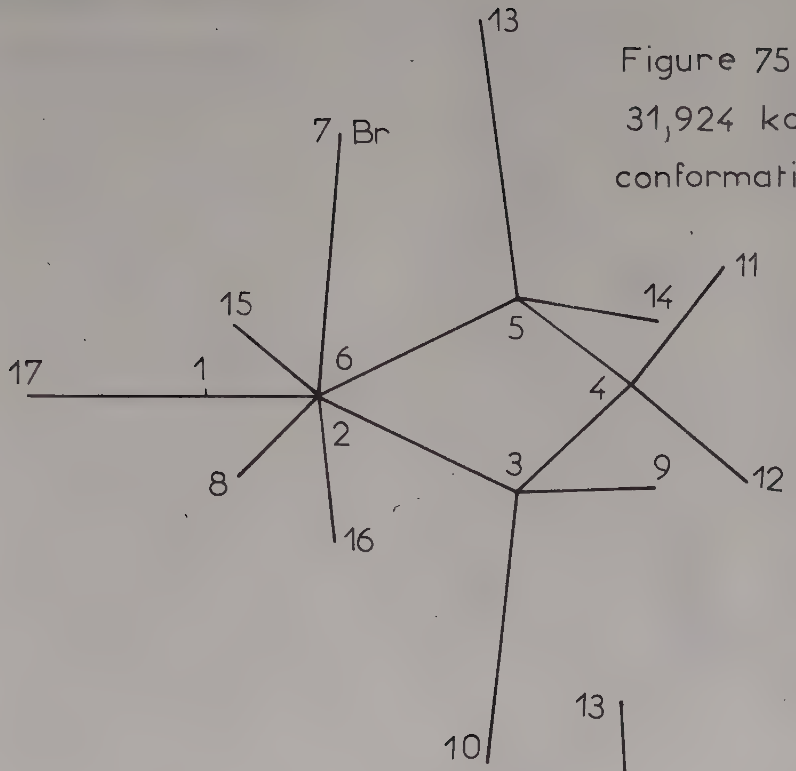


Figure 75
31,924 kcal.
conformation "croisée"

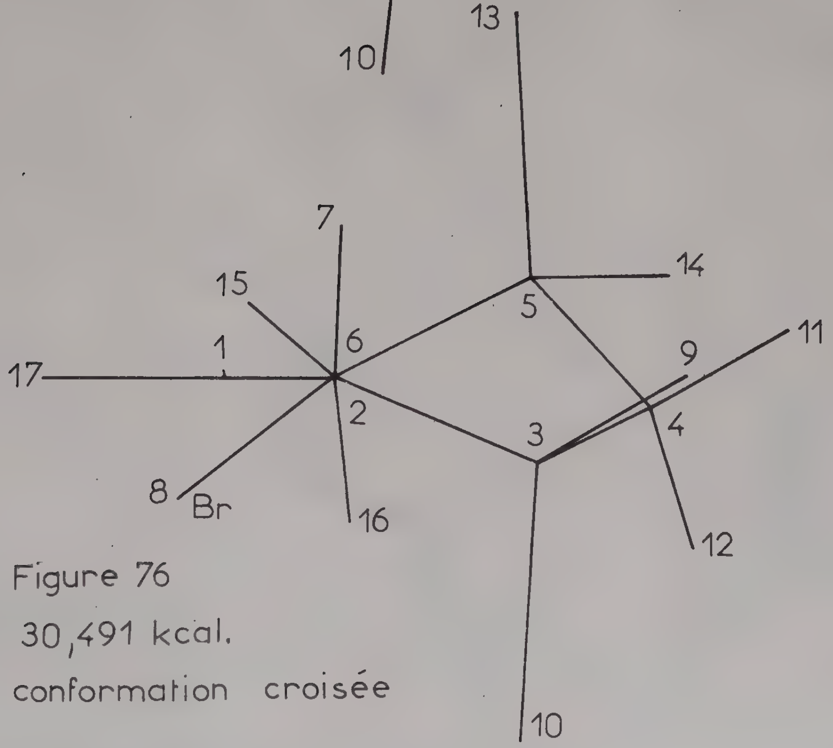


Figure 76
30,491 kcal.
conformation croisée

bromo-2 tétraméthyl-3,3,5,5 cyclohexanone

bromo-2
tétraméthyl-3,3,5,5
cyclohexanone. conformations
"bateau dissymétrique"

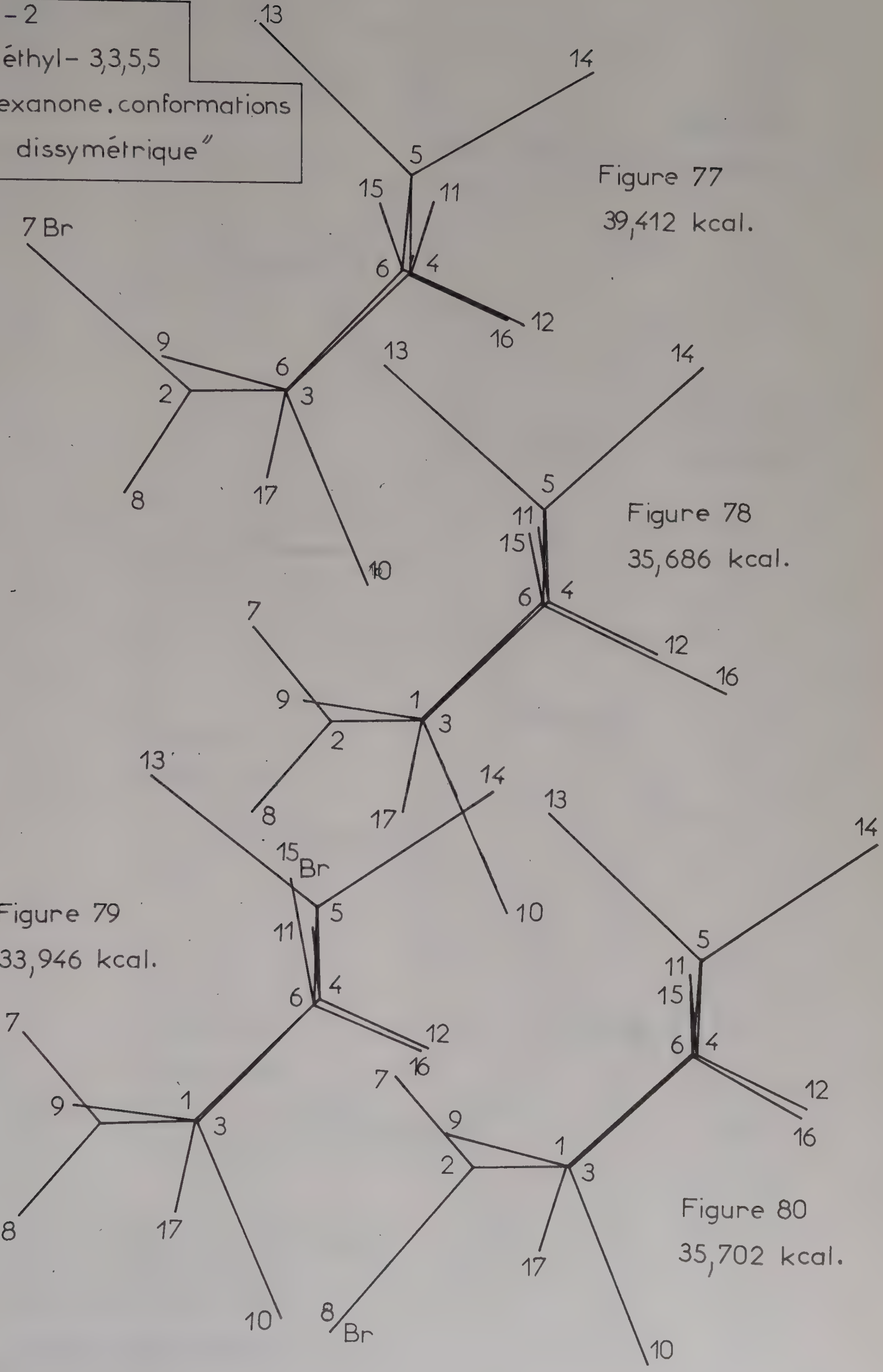


Figure 77
39,412 kcal.

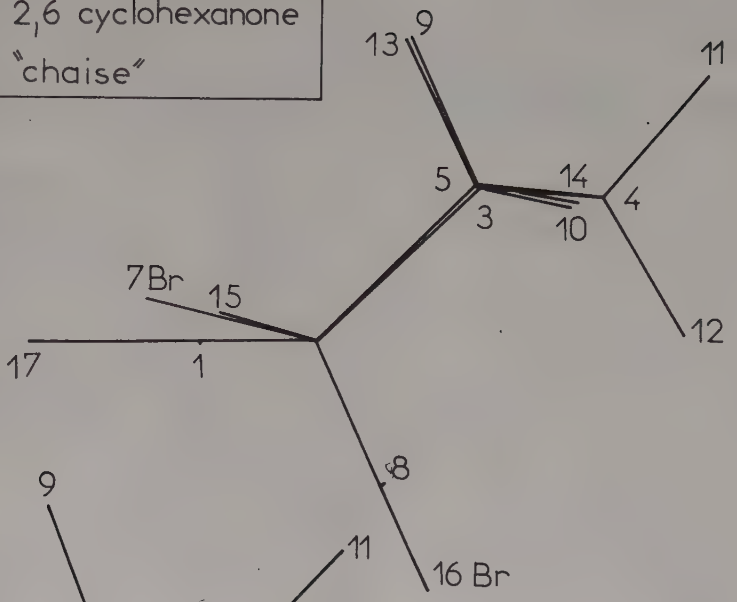
Figure 78
35,686 kcal.

Figure 79
33,946 kcal.

Figure 80
35,702 kcal.

trans dibromo-2,6 cyclohexanone
conformation "chaise"

Figure 85
10,651 kcal.



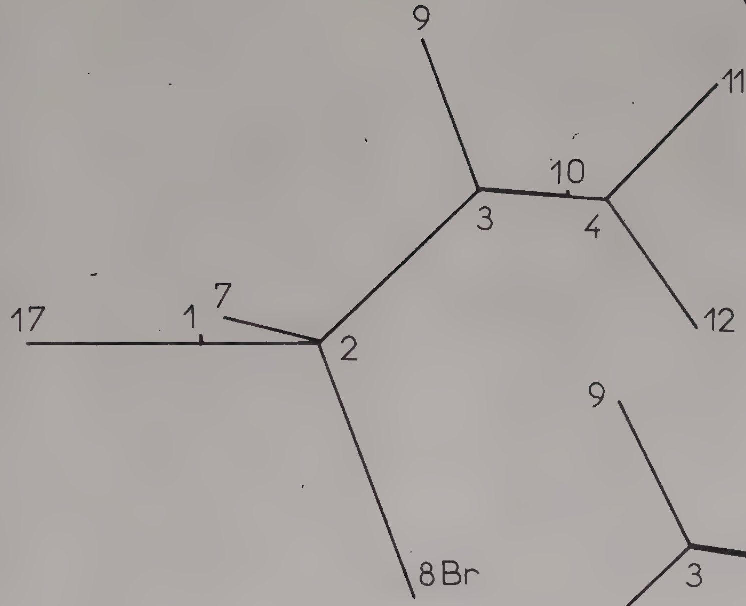


Figure 86
9,346 kcal.

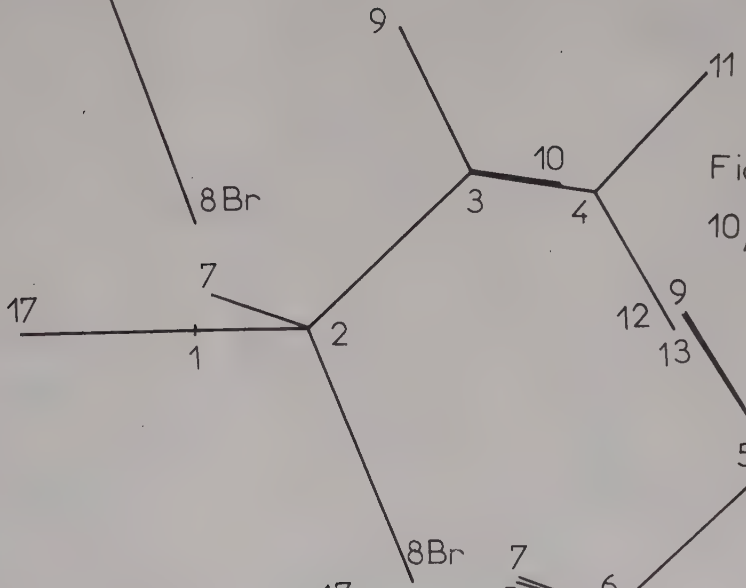


Figure 87
10,681 kcal.

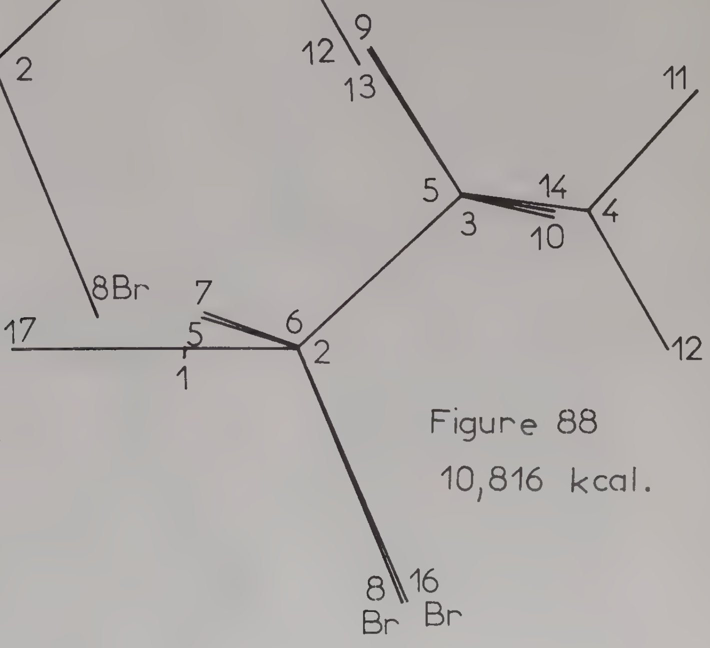


Figure 88
10,816 kcal.

cis dibromo-2,6
cyclohexanone
bromes diaxiaux
conformation "chaise"

dibromo-2,6 cyclohexanone
conformation "bateau"

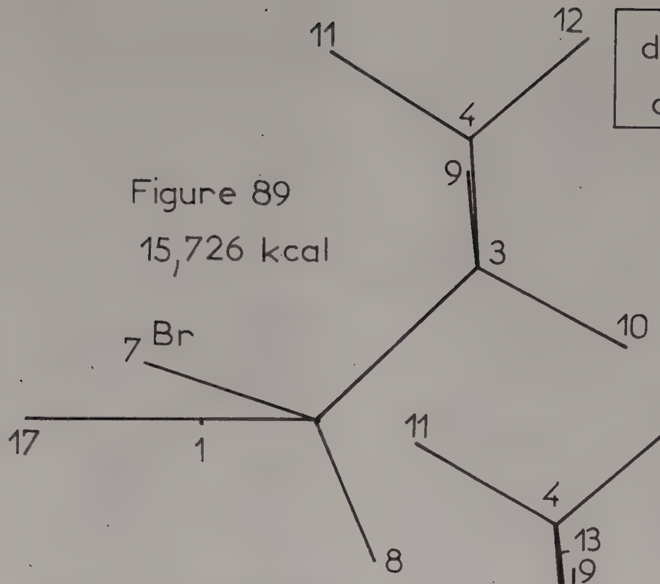


Figure 89
15,726 kcal

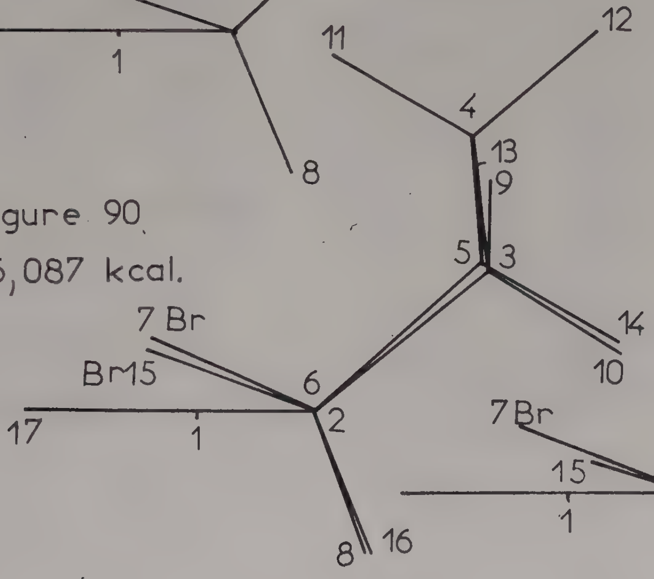


Figure 90
16,087 kcal.

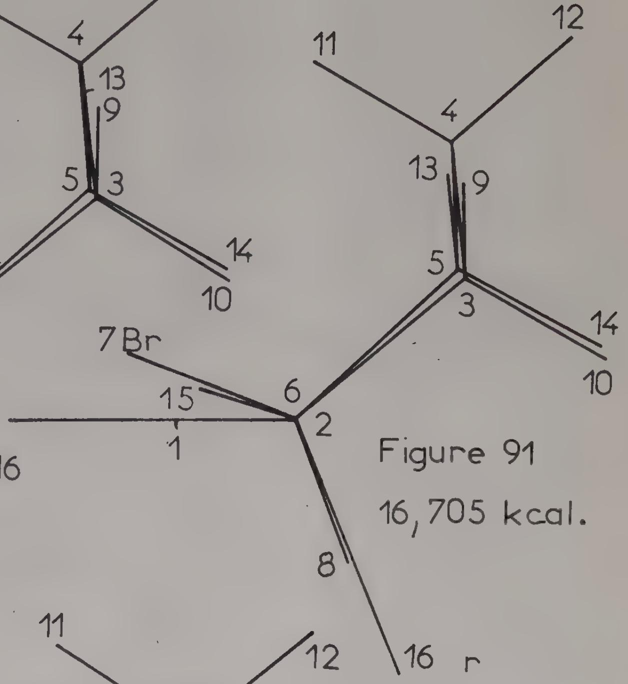


Figure 91
16,705 kcal.

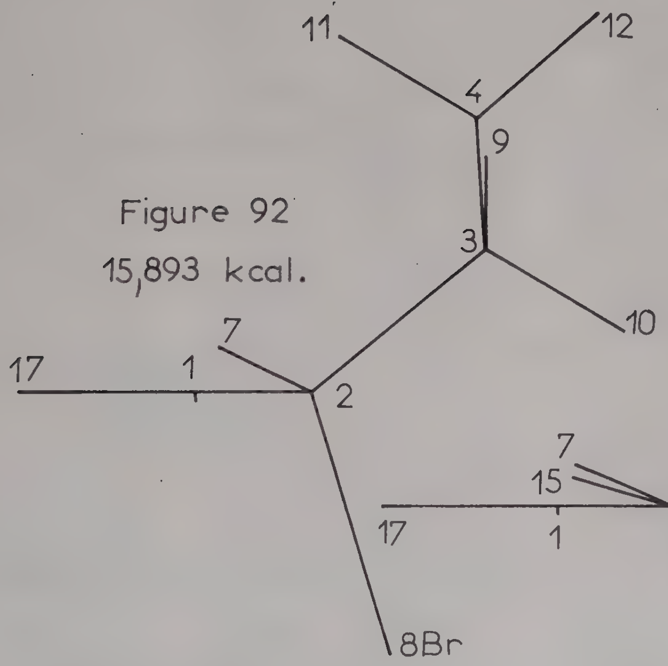


Figure 92
15,893 kcal.

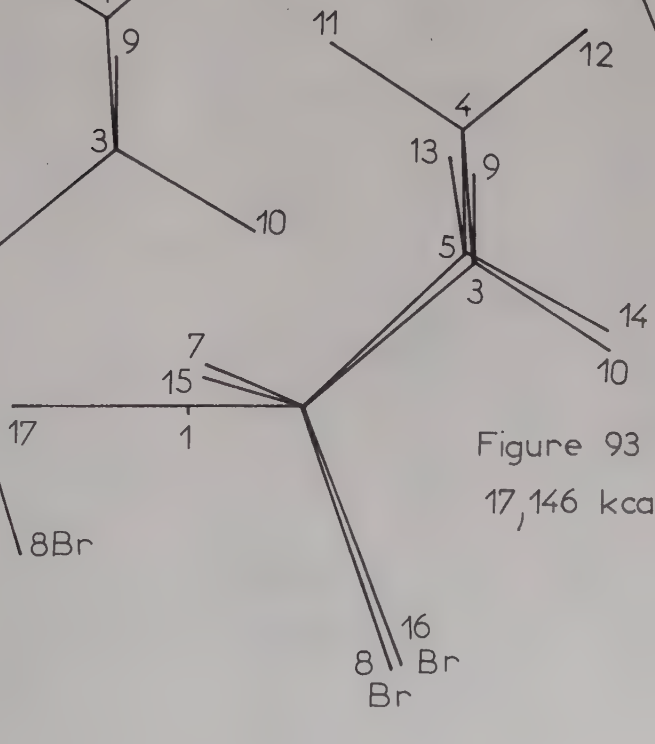


Figure 93
17,146 kcal.

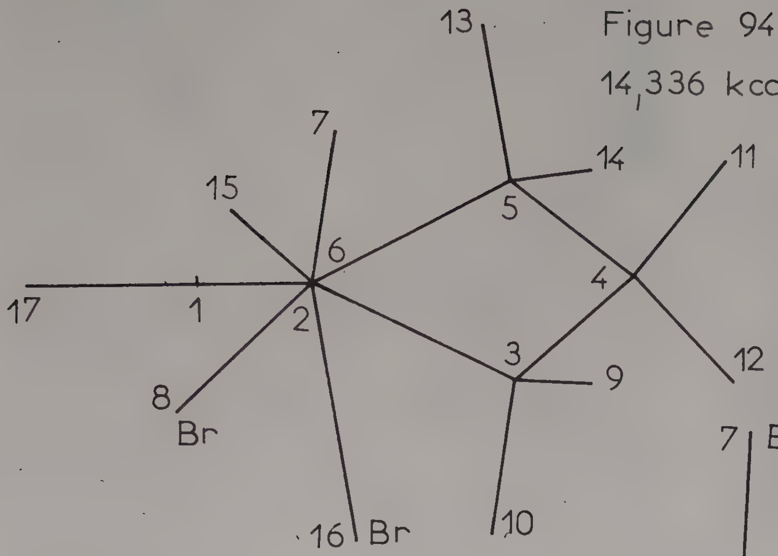


Figure 94

14,336 kcal.

conformation "croisée"

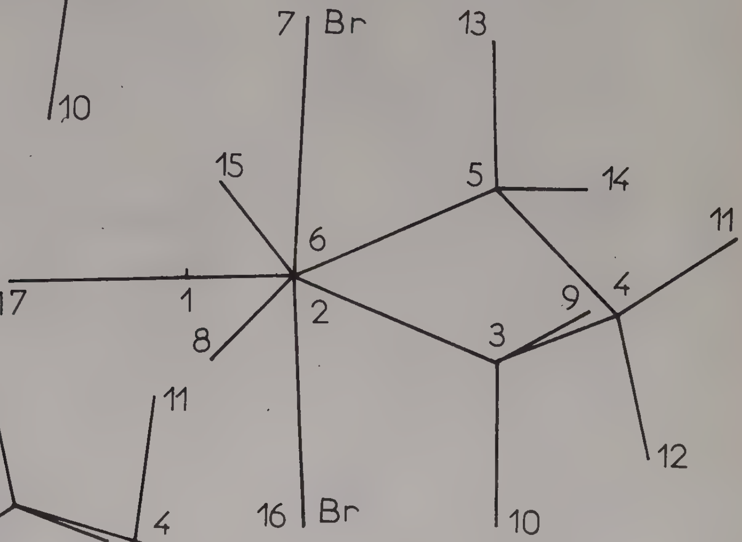


Figure 95

18,674 kcal.

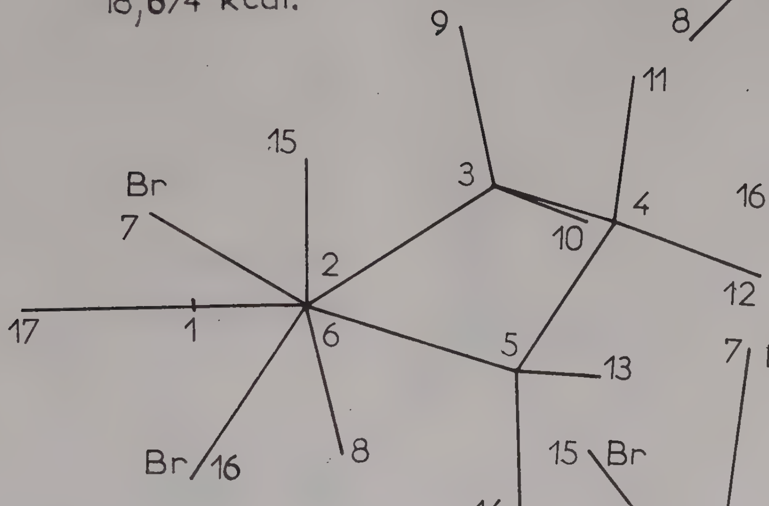


Figure 96

14,650 kcal.

conformations "bateau déformé"

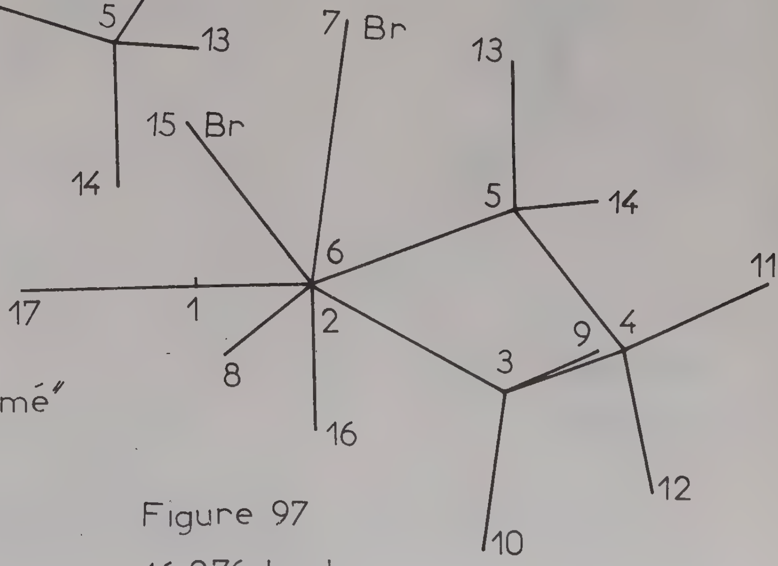


Figure 97

16,076 kcal.

dibromo-2,6
cyclohexanone

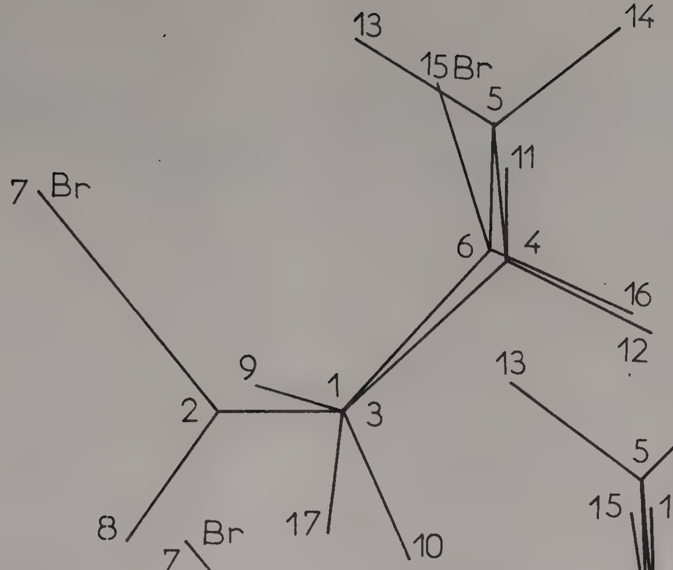


Figure 98
18,333 kcal.

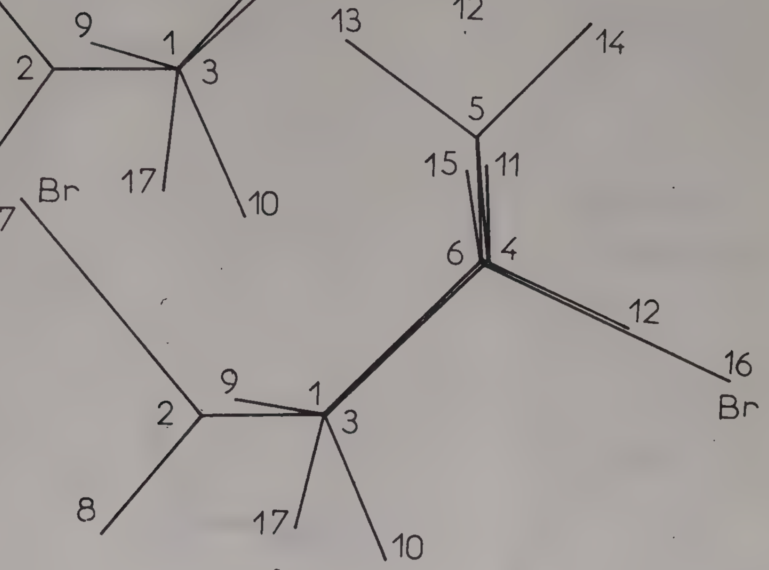


Figure 99
19,980 kcal.

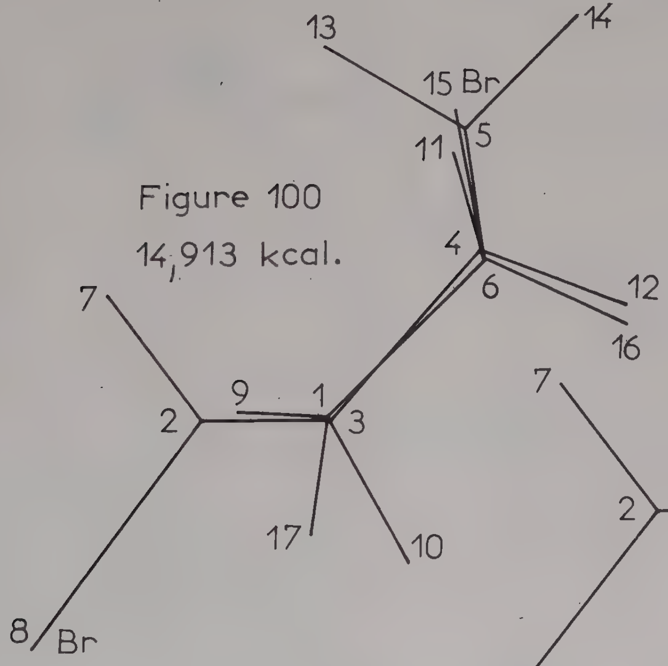


Figure 100
14,913 kcal.

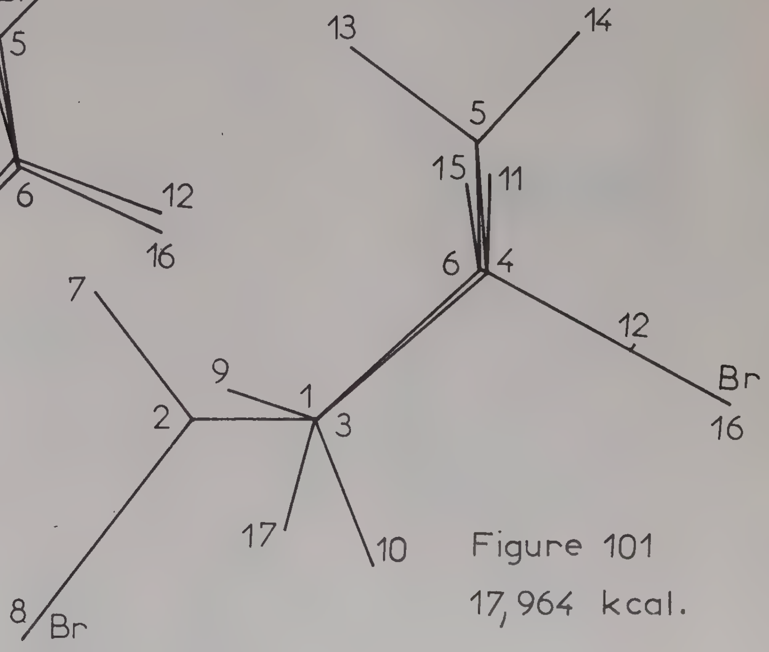


Figure 101
17,964 kcal.

dibromo-2,6 cyclohexanone
conformation "bateau dissymétrique"

cis dibromo-2,6 tétraméthyl-3,3,5,5 cyclohexanone
conformation "chaise"

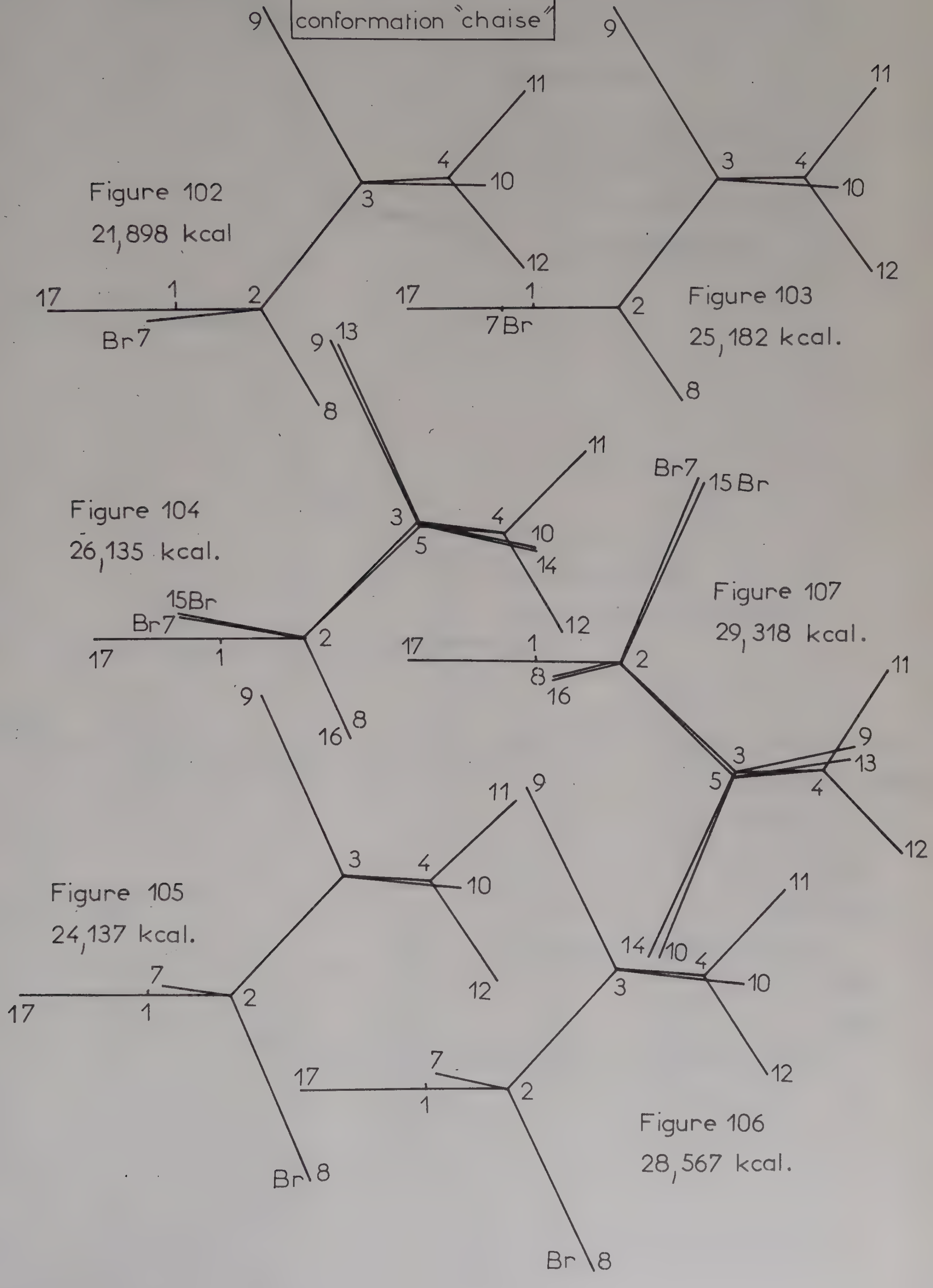


Figure 102
21,898 kcal

Figure 103
25,182 kcal.

Figure 104
26,135 kcal.

Figure 107
29,318 kcal.

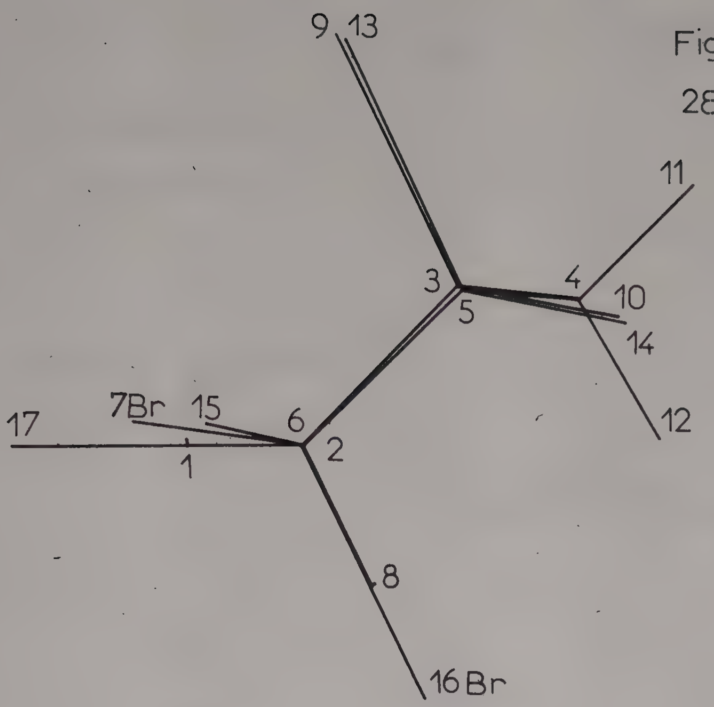
Figure 105
24,137 kcal.

Figure 106
28,567 kcal.

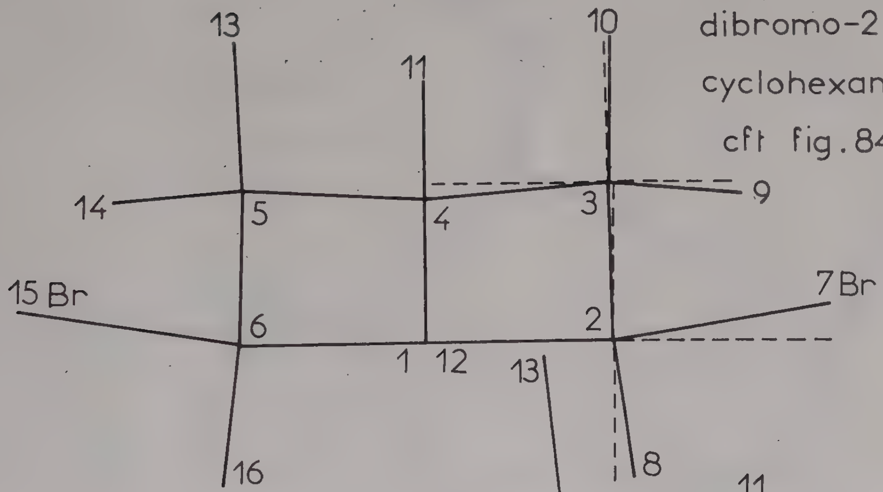
Figure 108

28,567 kcal.

transdibromo-2,6
tétraméthyl-3,3,5,5
cyclohexanone



dibromo-2,6
cyclohexanone
cft fig. 84 9,050 kcal.



dibromo-2,6
tétraméthyl-3,3,5,5
cyclohexanone
cft fig 104
26,135 kcal.

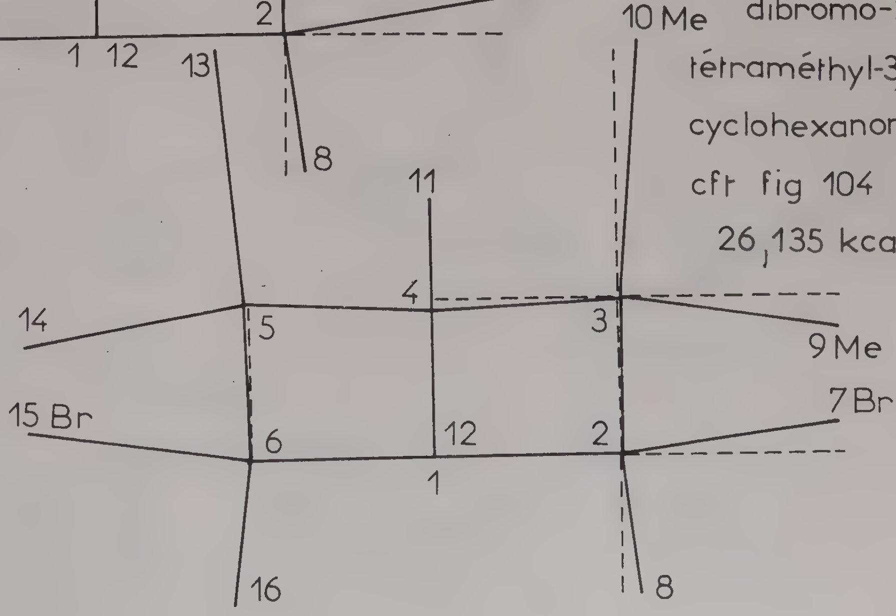


Figure 109
projections dans
le plan x z

dibromo-2,6 tétraméthyl 3,3,5,5 cyclohexanone
conformations "bateau symétrique"

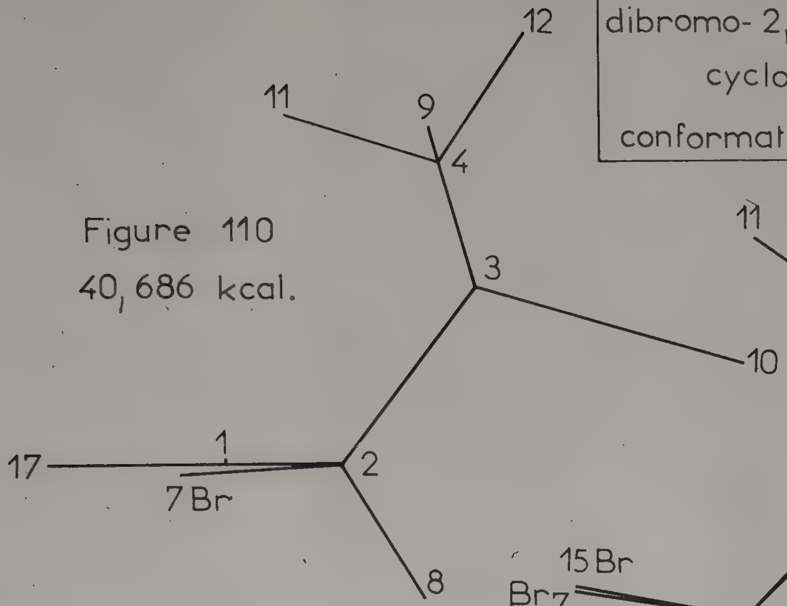


Figure 110
40,686 kcal.

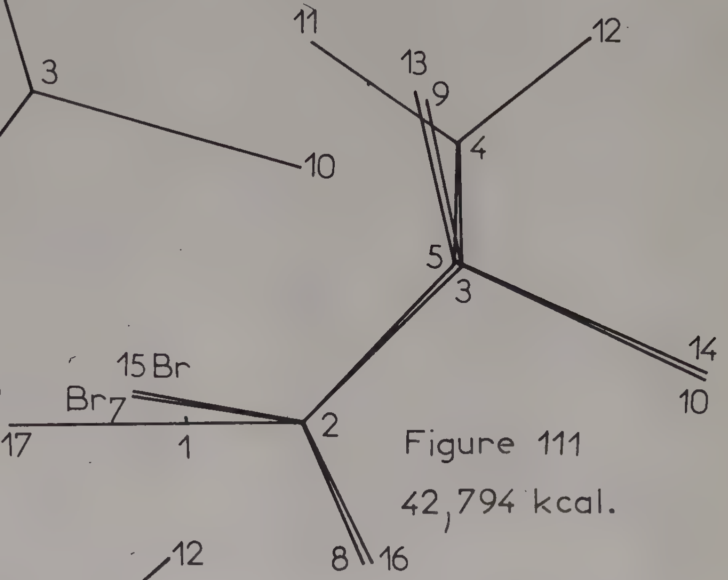


Figure 111
42,794 kcal.

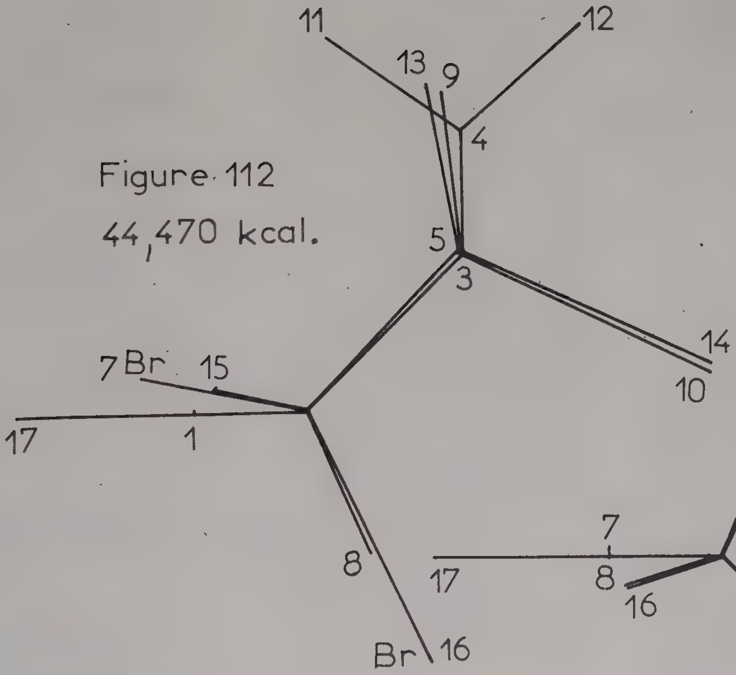


Figure 112
44,470 kcal.

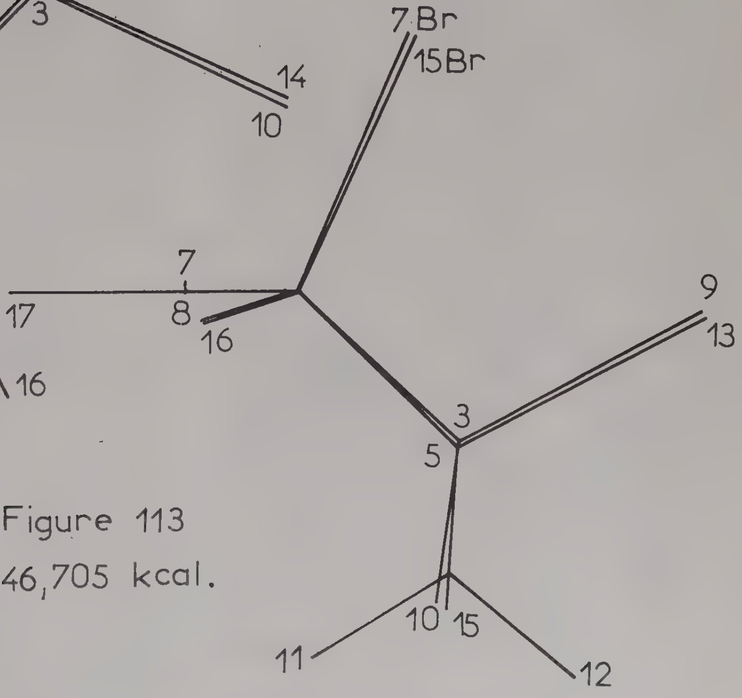


Figure 113
46,705 kcal.

dibromo-2,6 tétraméthyl 3,3,5,5 cyclohexanone. conformations "croisée" et "bateau déformé"

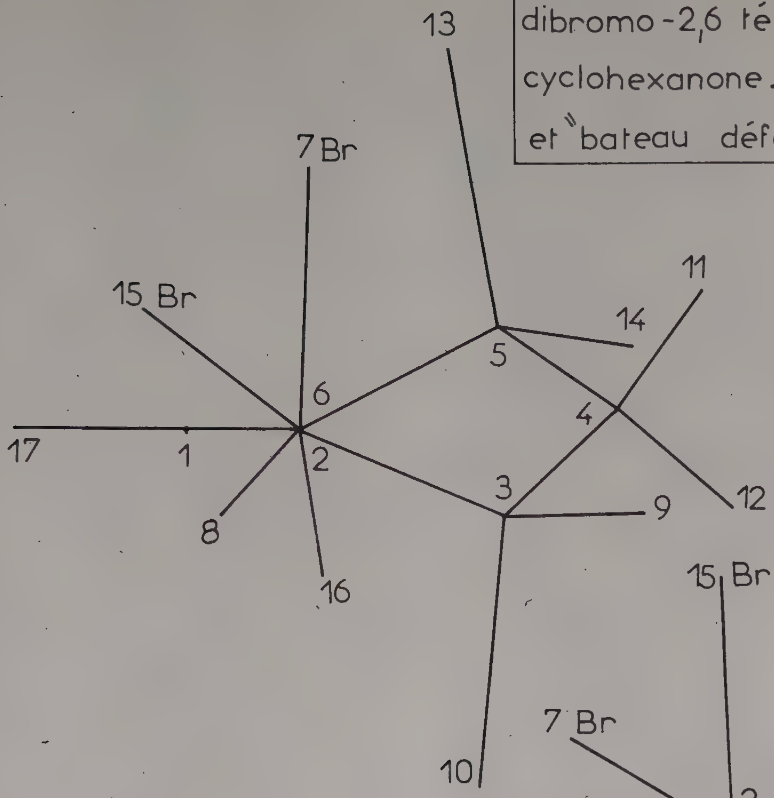


Figure 114 36,445 kcal.

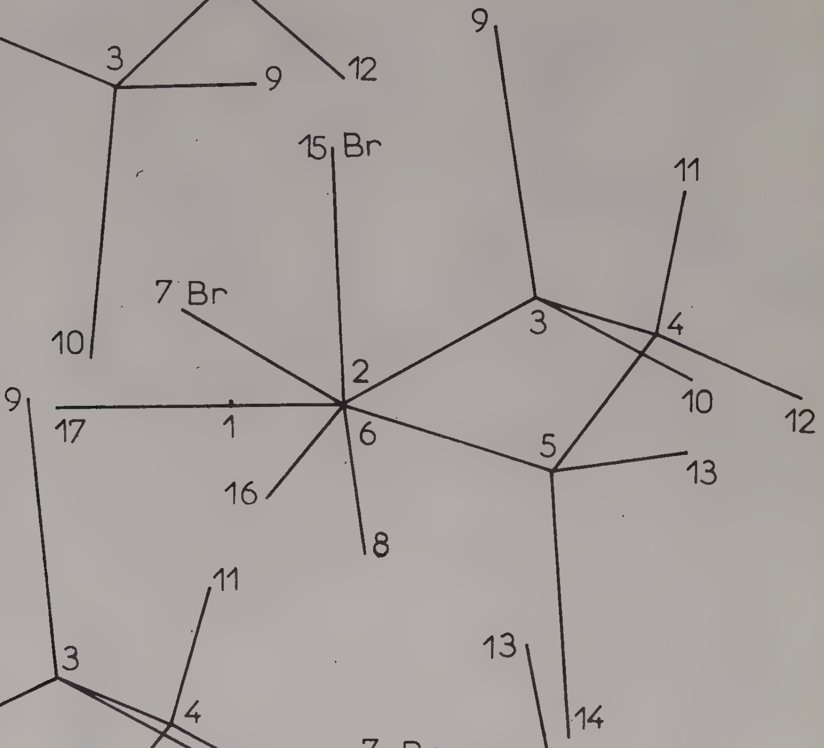


Figure 115
35,902 kcal.

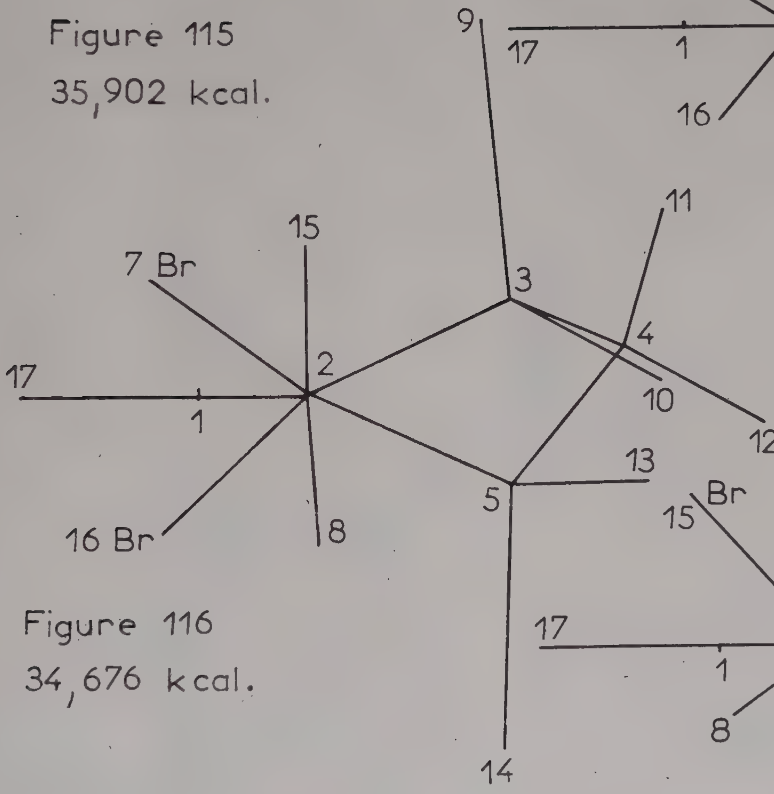


Figure 116
34,676 kcal.

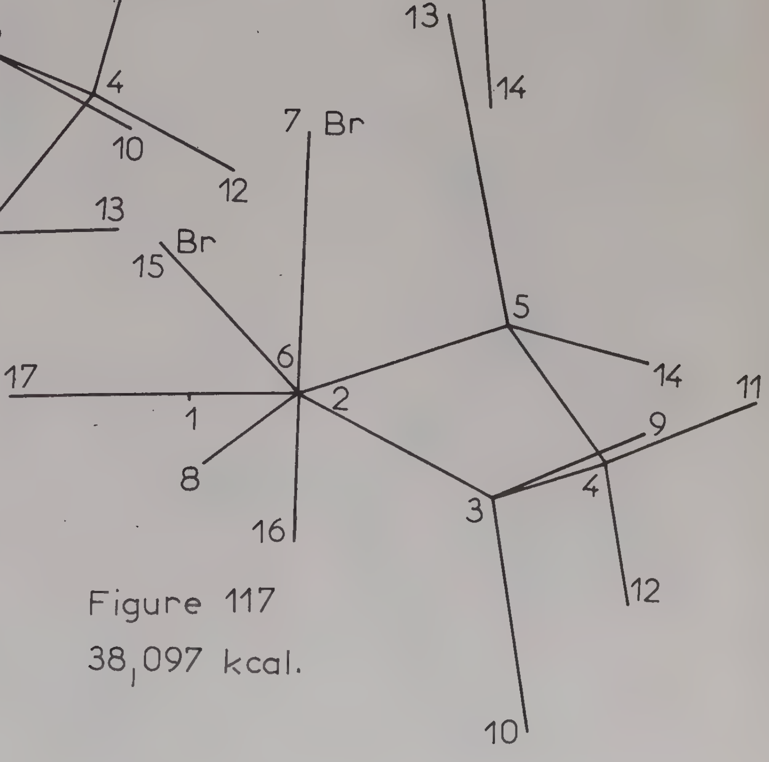


Figure 117
38,097 kcal.

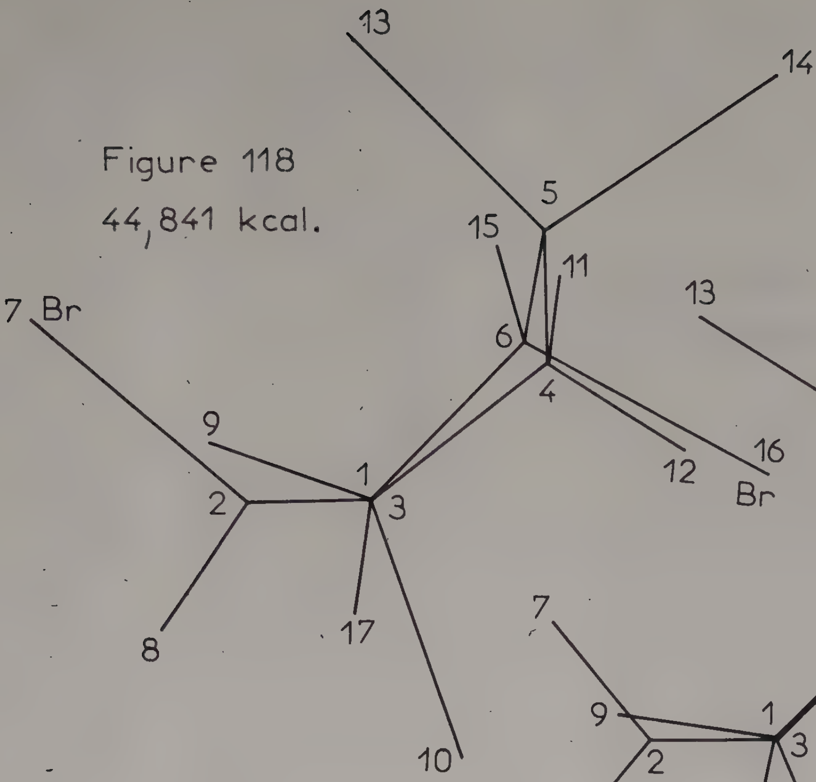


Figure 118
44,841 kcal.

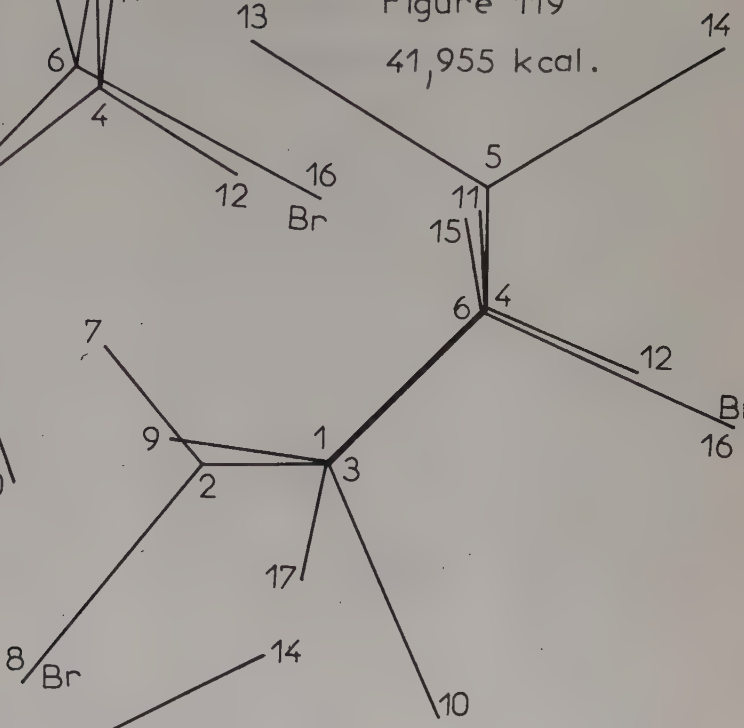


Figure 119
41,955 kcal.

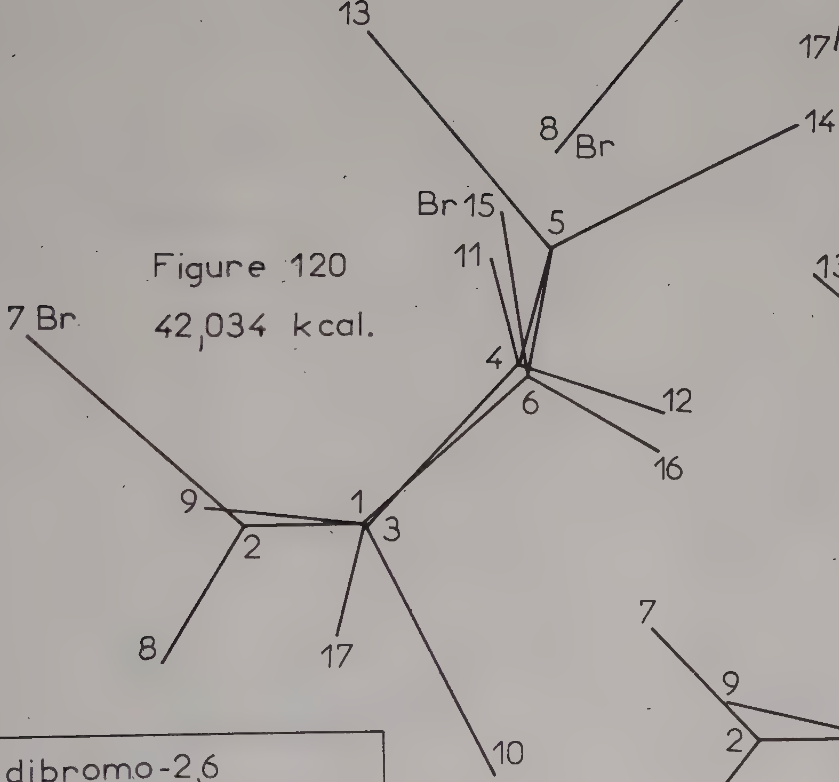


Figure 120
42,034 kcal.

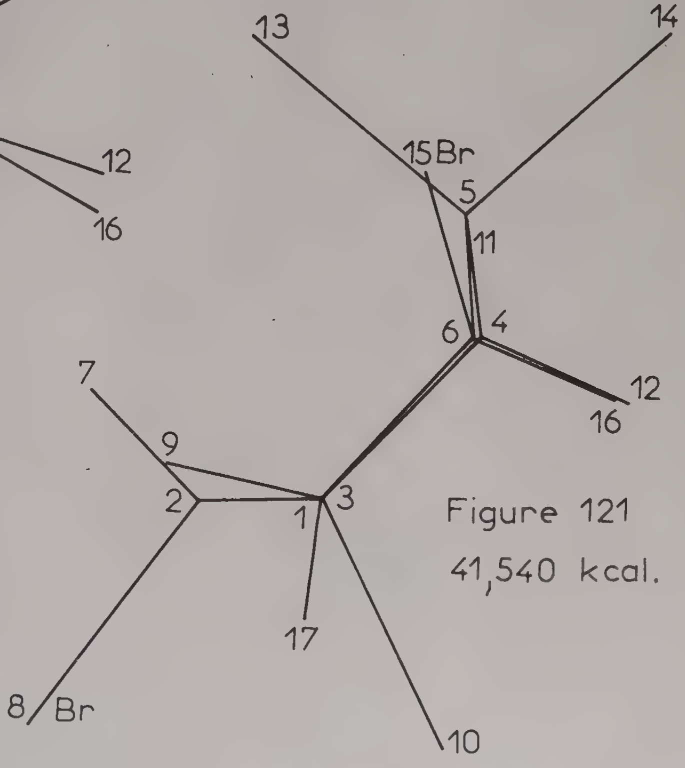


Figure 121
41,540 kcal.

dibromo-2,6
tétraméthyl - 3,3,5,5
cyclohexanone. conformations
"bateau dissymétrique"

dimethyl-6,6 bicyclo [3.1.1] heptane

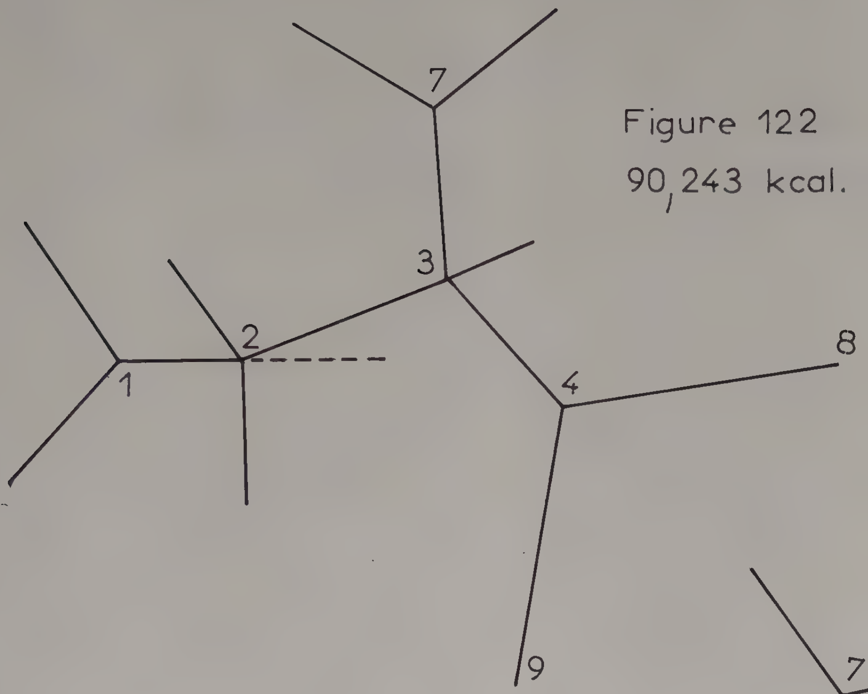


Figure 122
90,243 kcal.

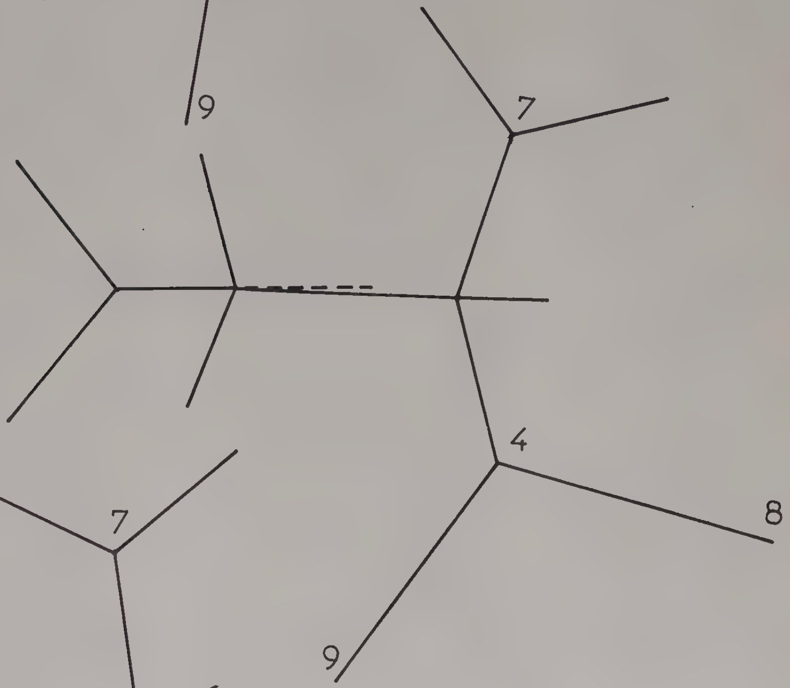


Figure 123
95,153 kcal.

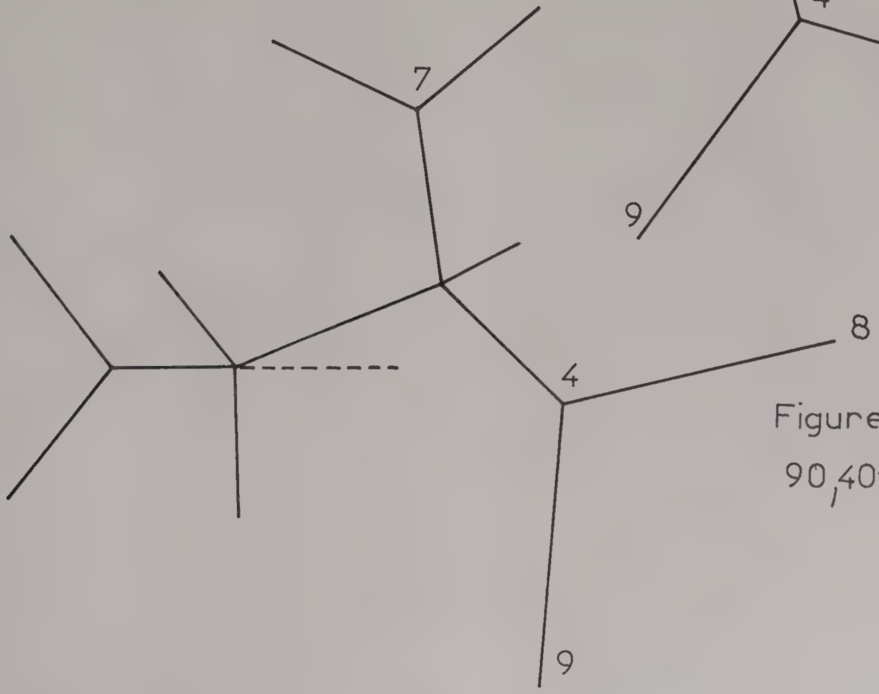


Figure 124
90,401 kcal.

diméthyl-6,6 bicyclo [3.1.1] heptane

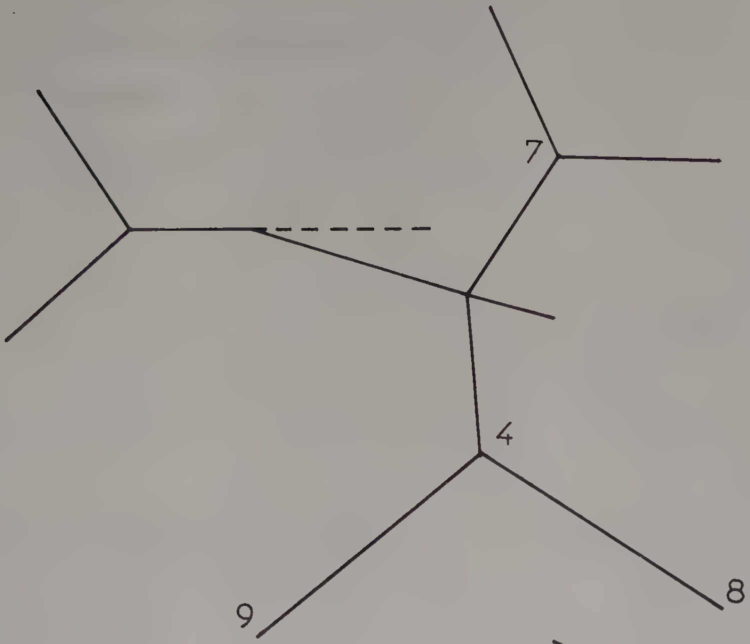


Figure 125
95,758 kcal.

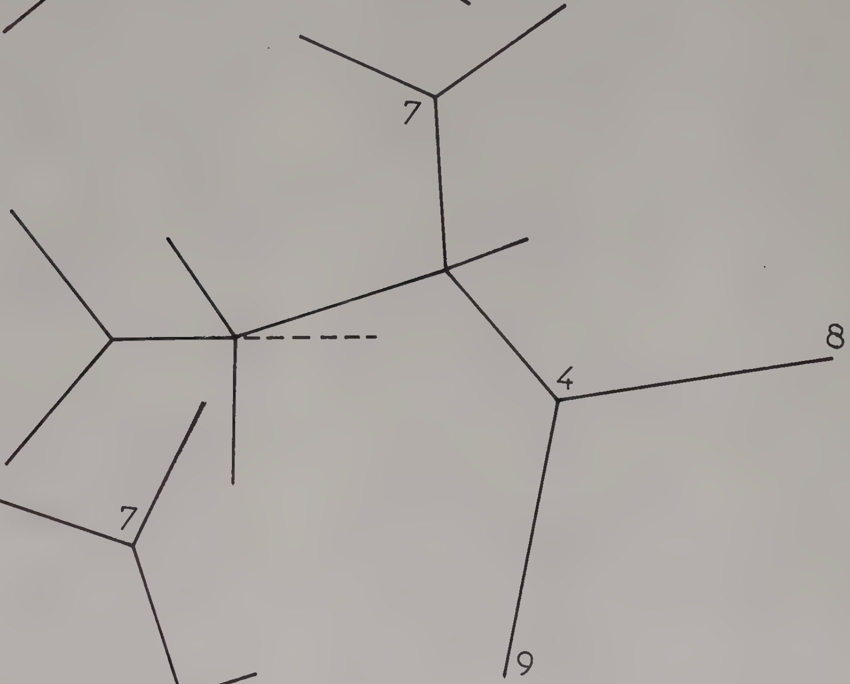


Figure 126
87,097 kcal.

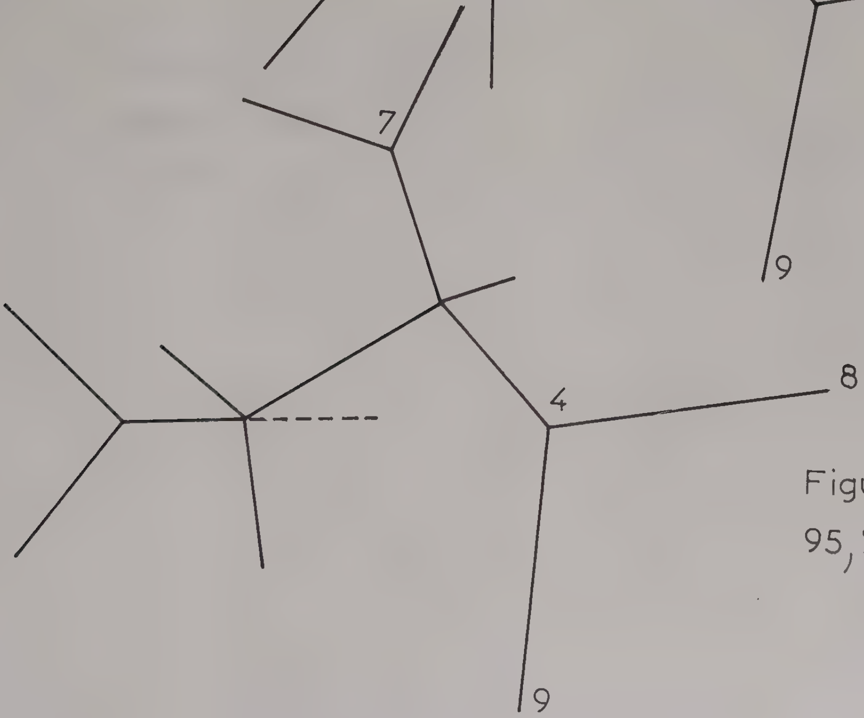
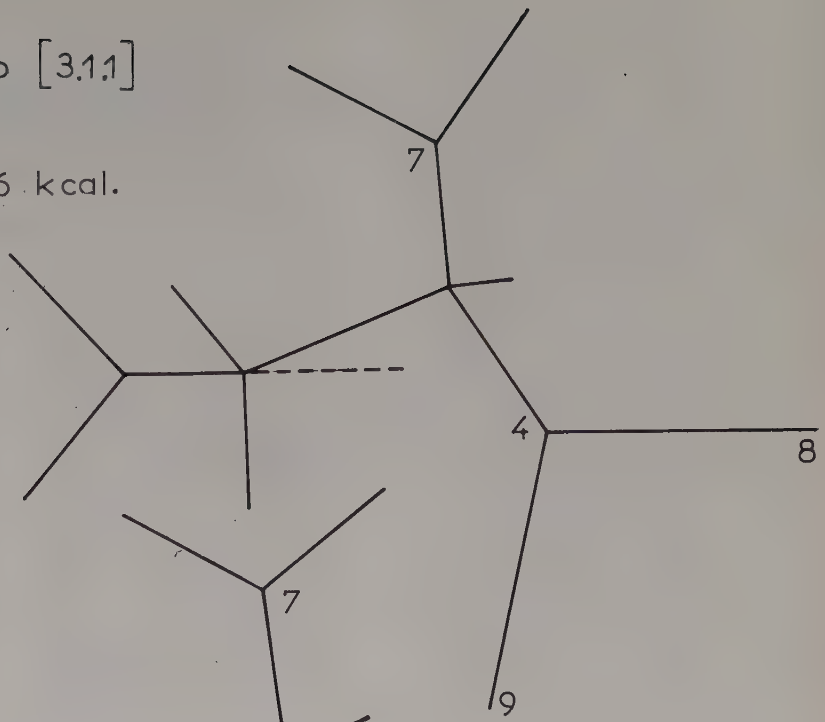
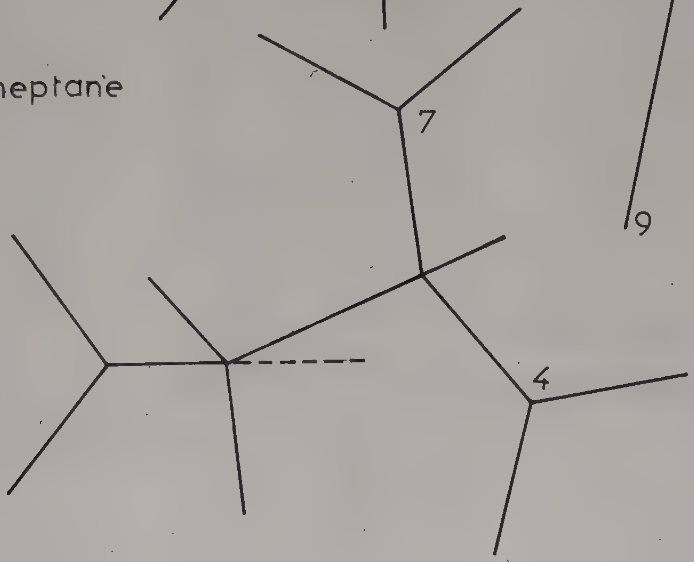


Figure 127
95,787 kcal.

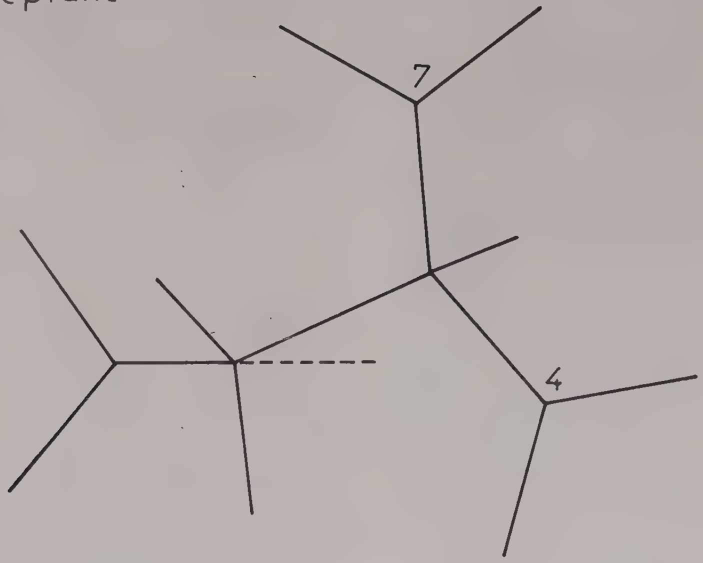
diméthyl-6,6 bicyclo [3.1.1] heptane
Figure 128 90,876 kcal.



bicyclo [3.1.1] heptane
Figure 129
73,857 kcal.



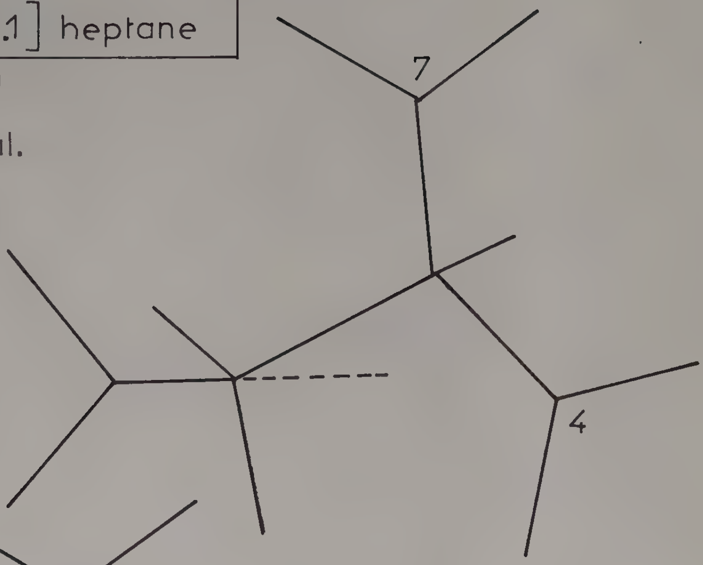
bicyclo [3.1.1] heptane
Figure 130
73,607 kcal.



bicyclo [3.1.1] heptane

Figure 131

69,836 kcal.



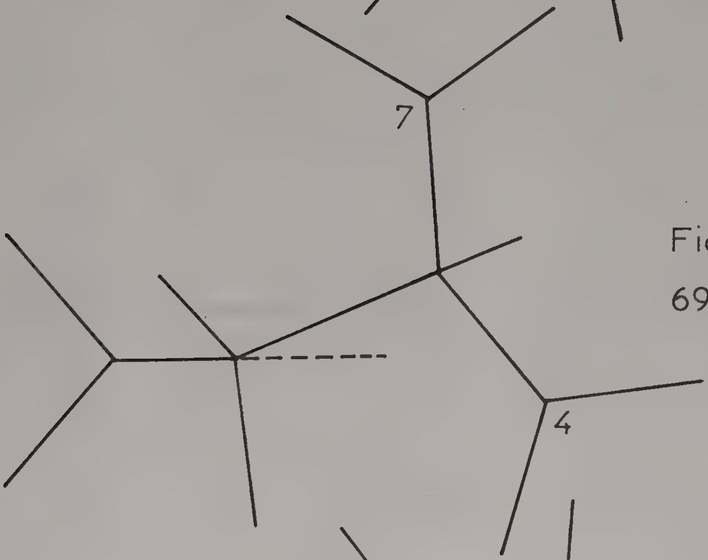
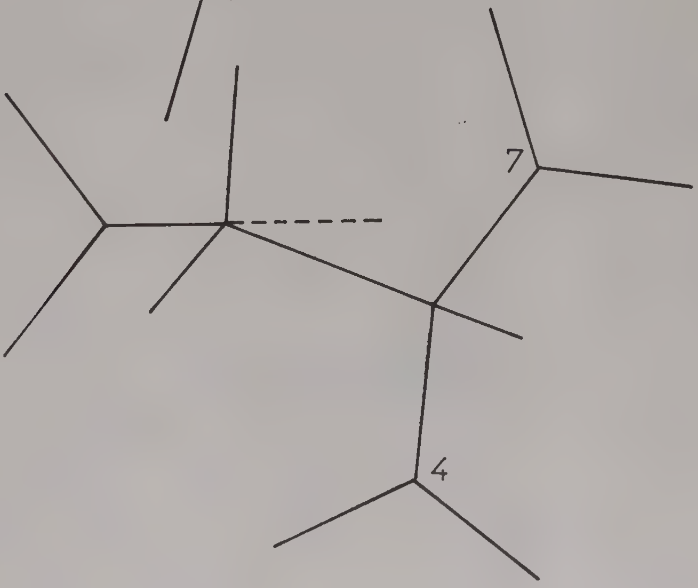


Figure 132

69,842 kcal.

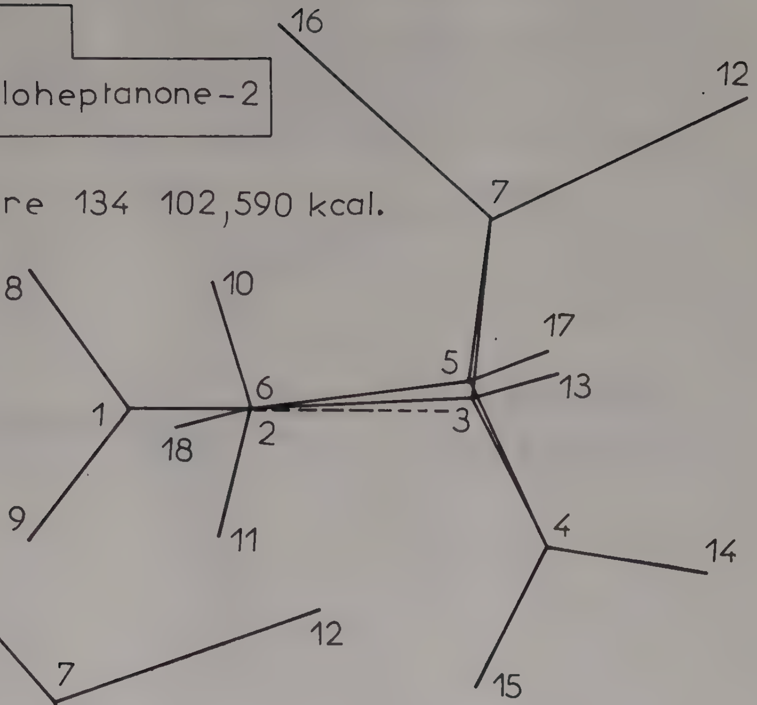
Figure 133

72,739 kcal.



diméthyl-6,6
bicyclo [3.1.1] bicycloheptanone-2

Figure 134 102,590 kcal.



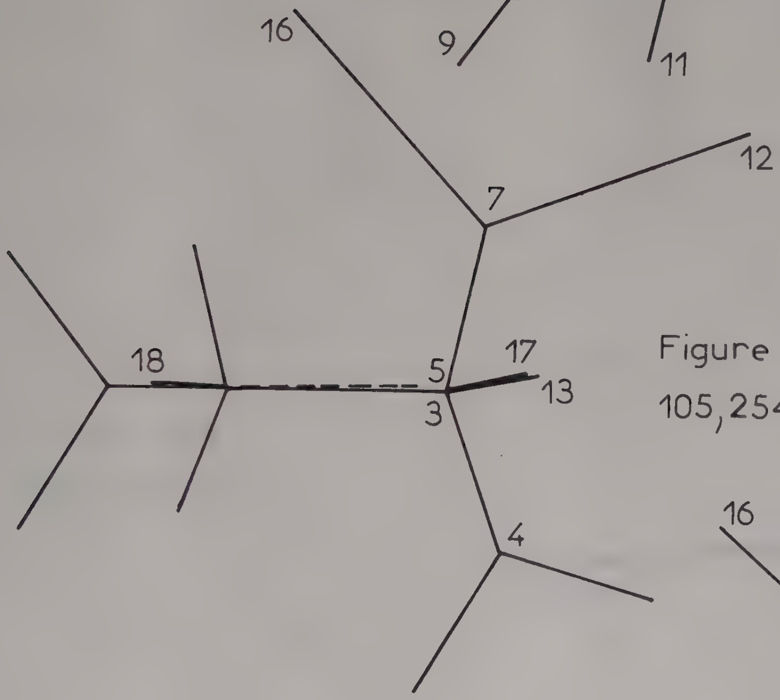


Figure 135
105,254 kcal.

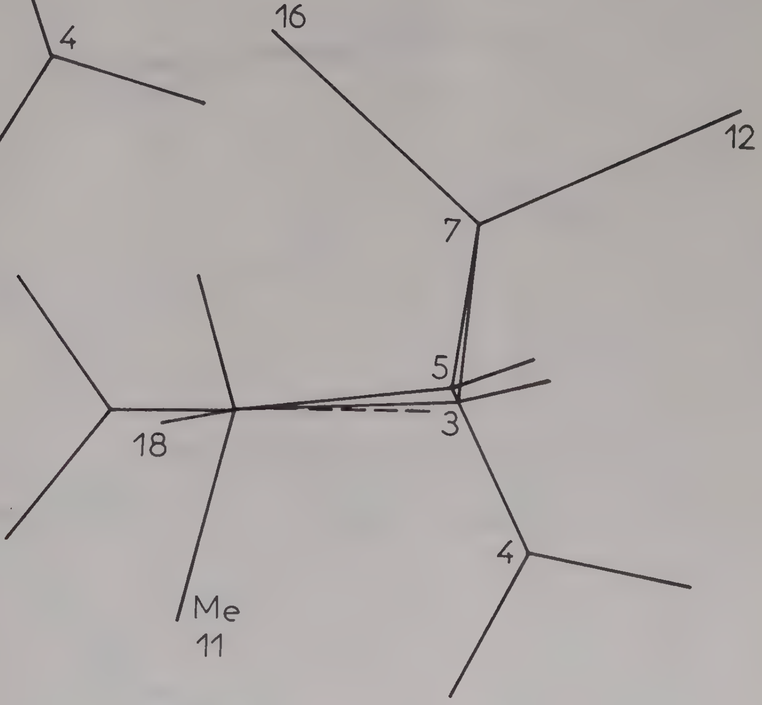


Figure 136 106,823 kcal.

triméthyl-4,6,6
bicyclo [3.1.1]
heptanone-2

triméthyl-4,6,6 bicyclo [3.1.1] heptanone-2

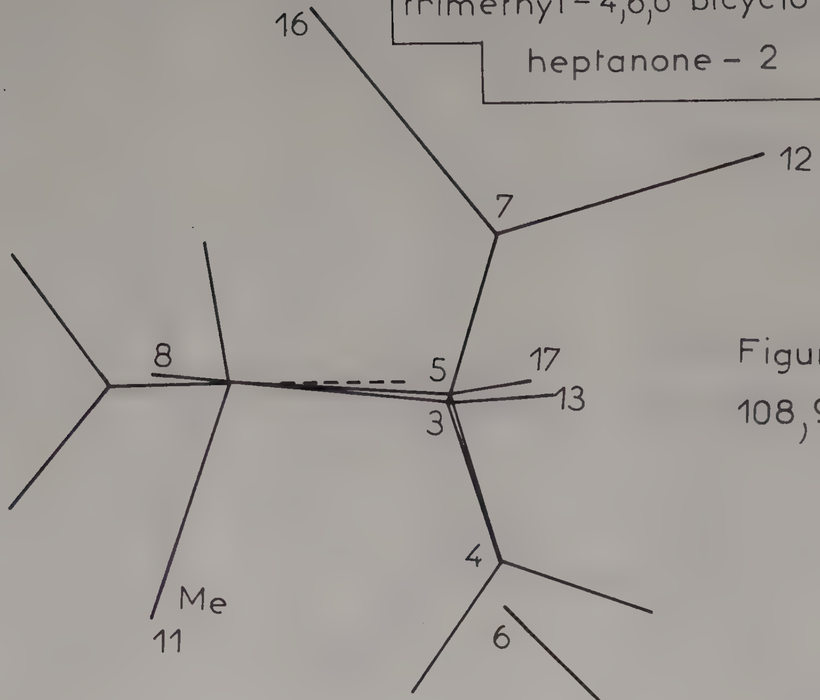


Figure 137
108,903 kcal.

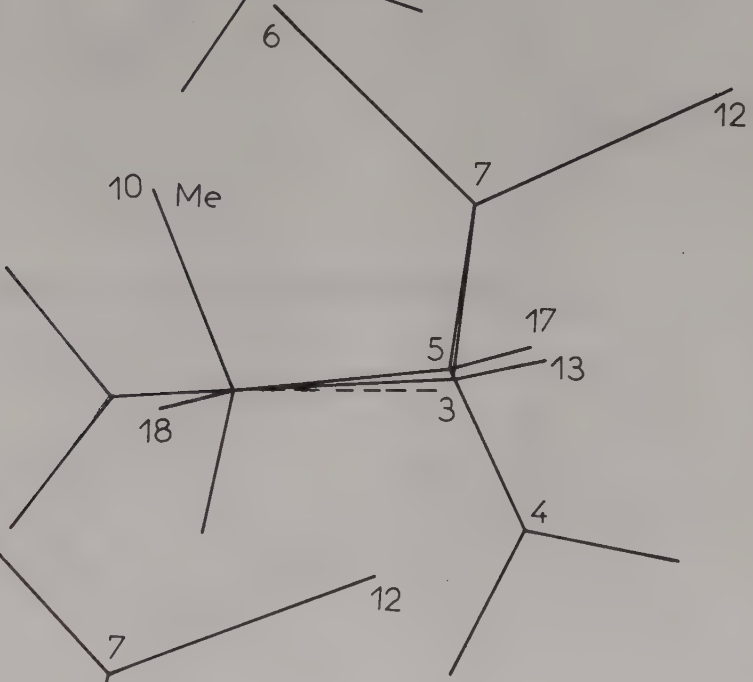


Figure 138
109,425 kcal.

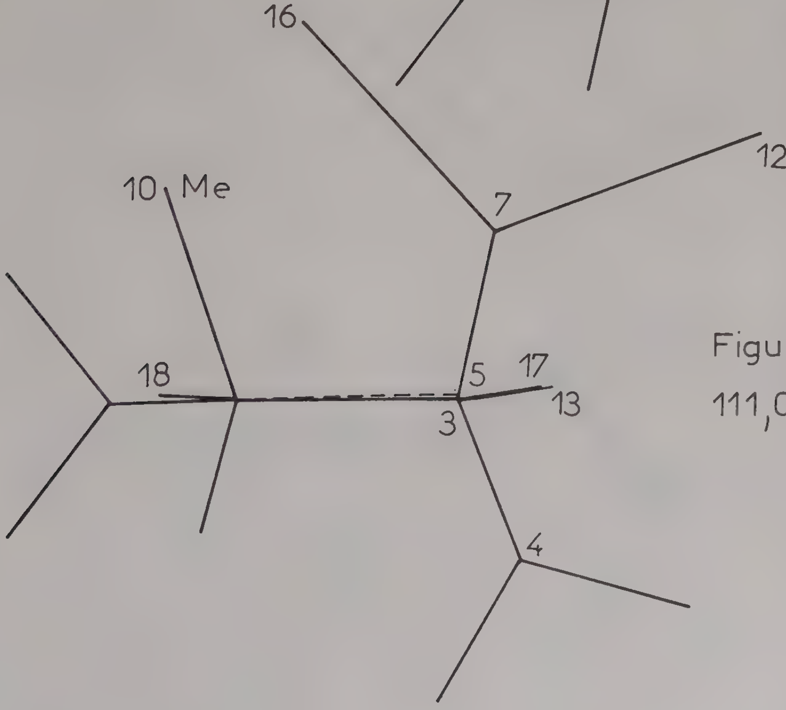


Figure 139
111,078 kcal.

diméthyl-6,6
bicyclo [3.1.1] heptanone -3

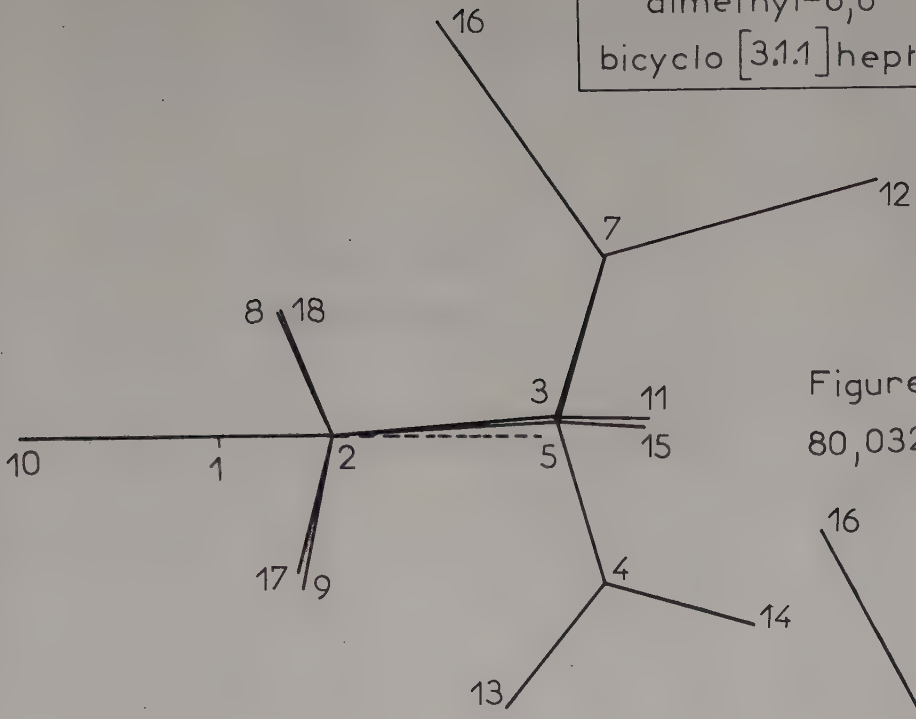


Figure 140
80,032 kcal.

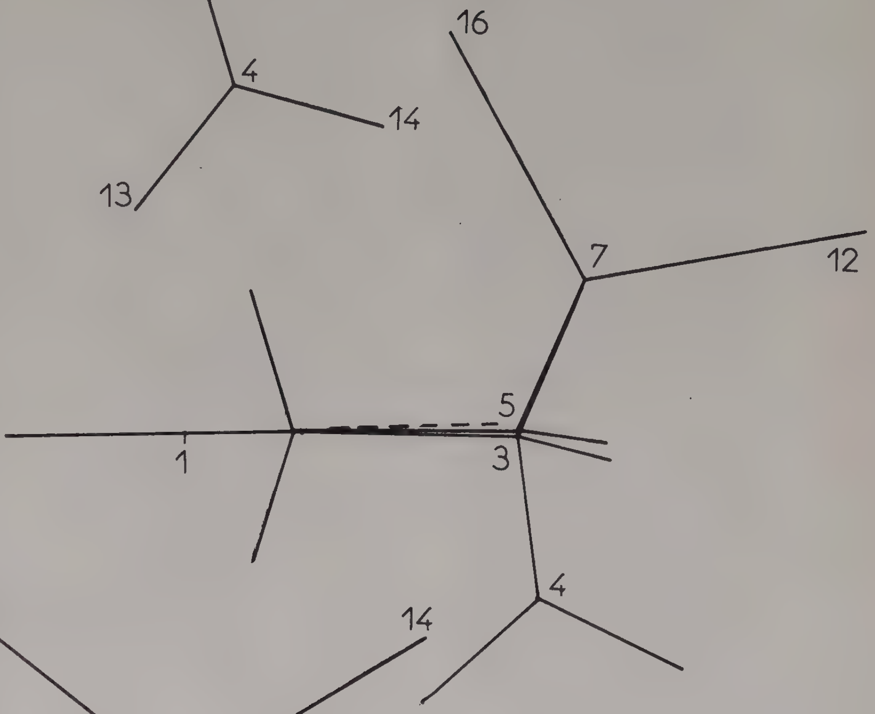


Figure 141
81,463 kcal.

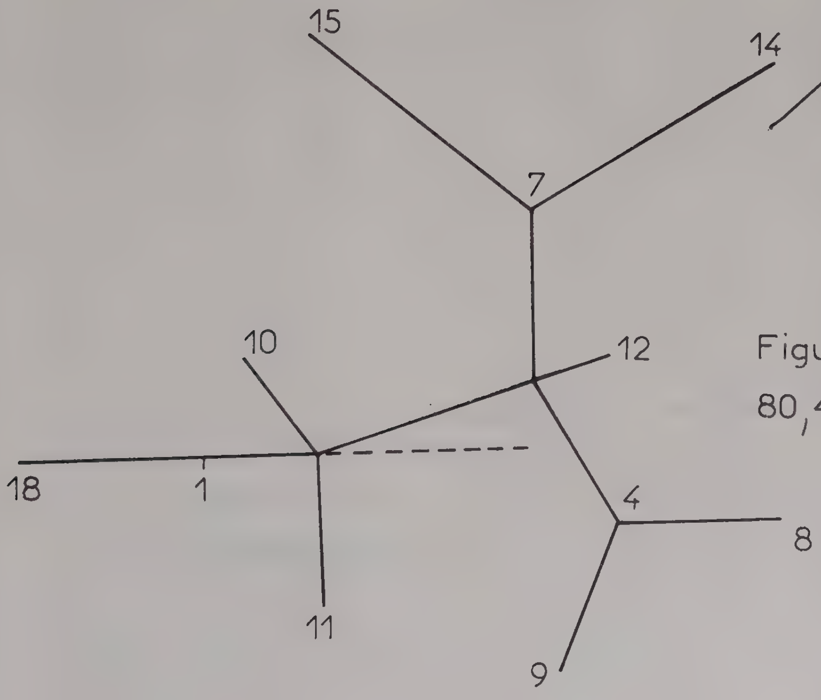


Figure 142
80,484 kcal

dimérhyl-6,6 bicyclo [3.1.1] heptanone-3

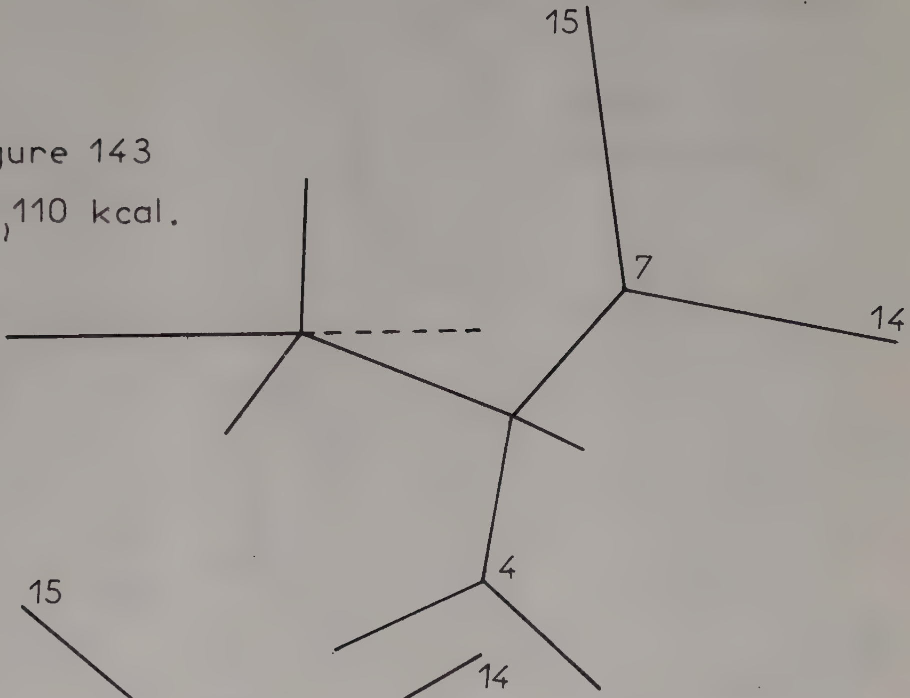


Figure 143
83,110 kcal.

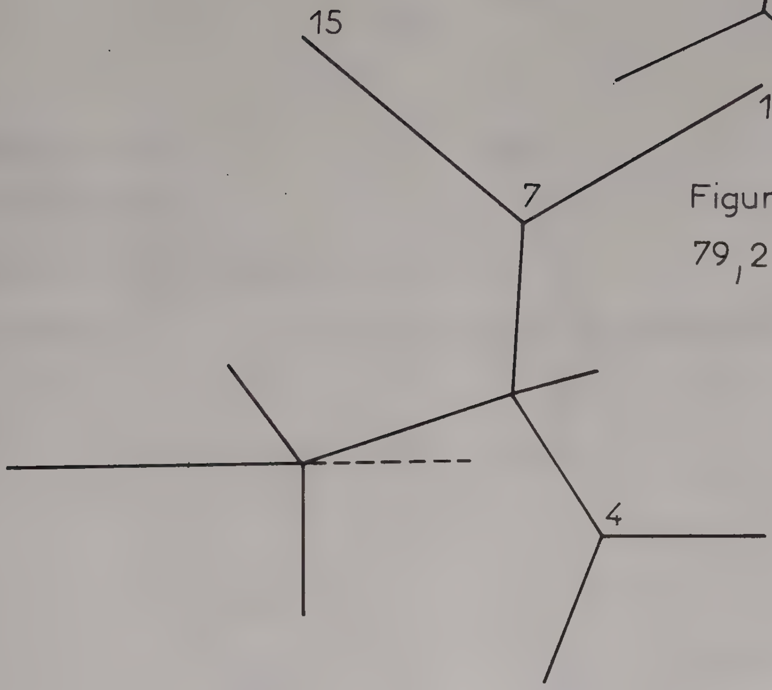


Figure 144
79,291 kcal.

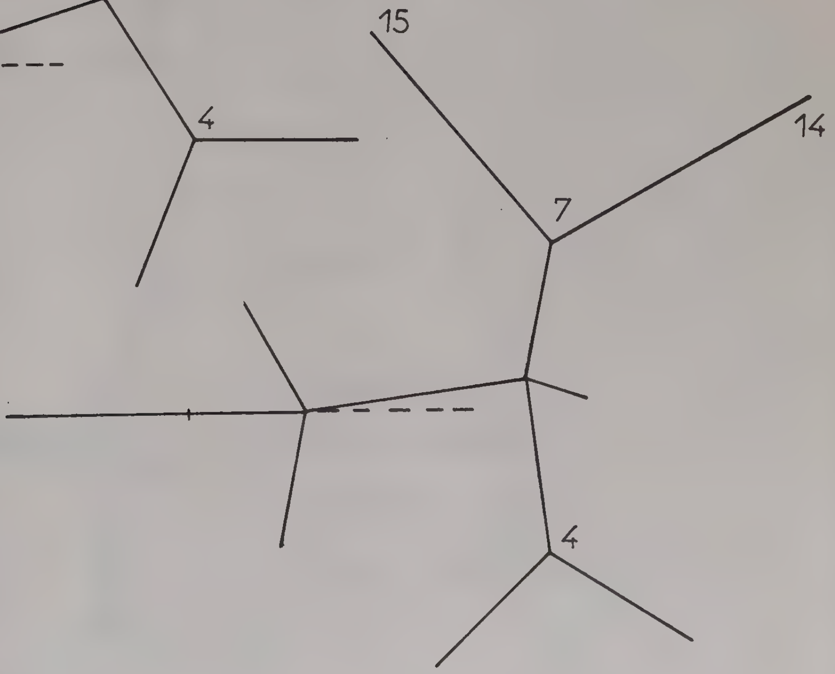


Figure 145
83,686 kcal.

diméthyl - 6,6 bicyclo [3.1.1] heptanone - 3

Figure 146

82,835 kcal.

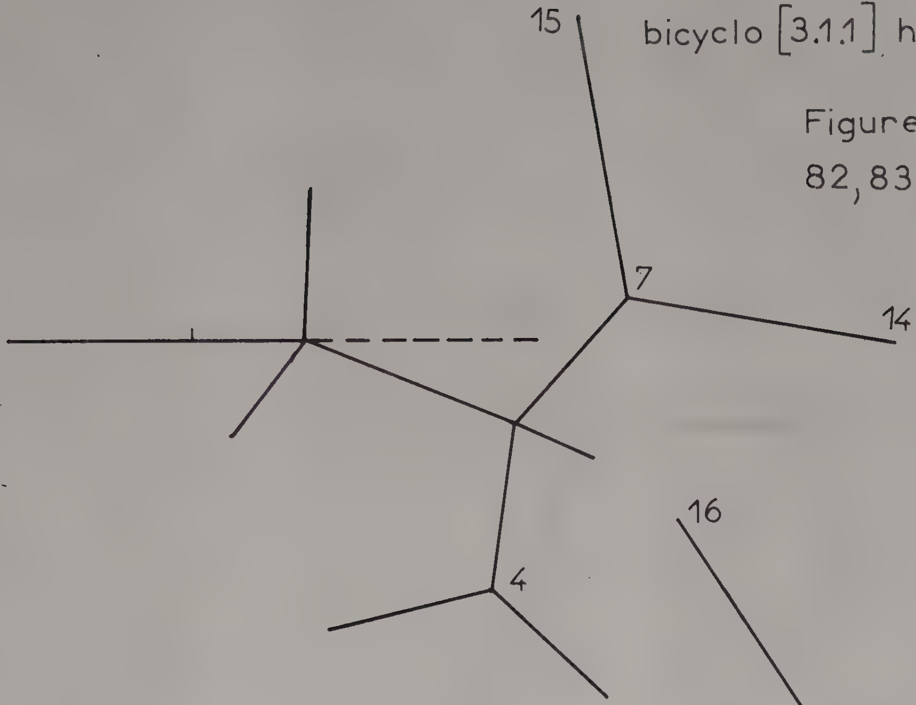
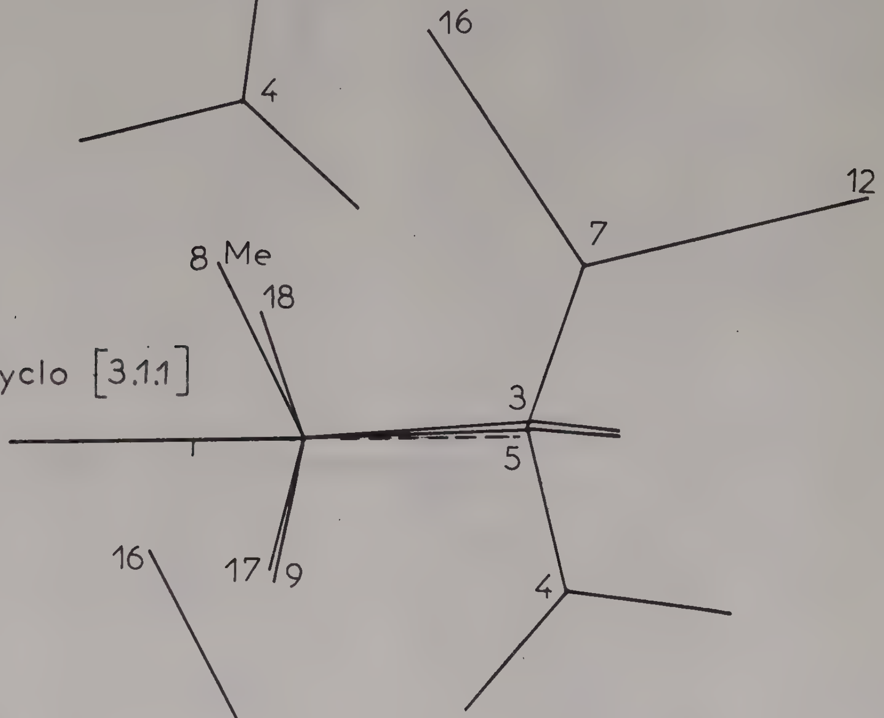


Figure 147

82,831 kcal.

triméthyl - 2,6,6 bicyclo [3.1.1] heptanone - 3



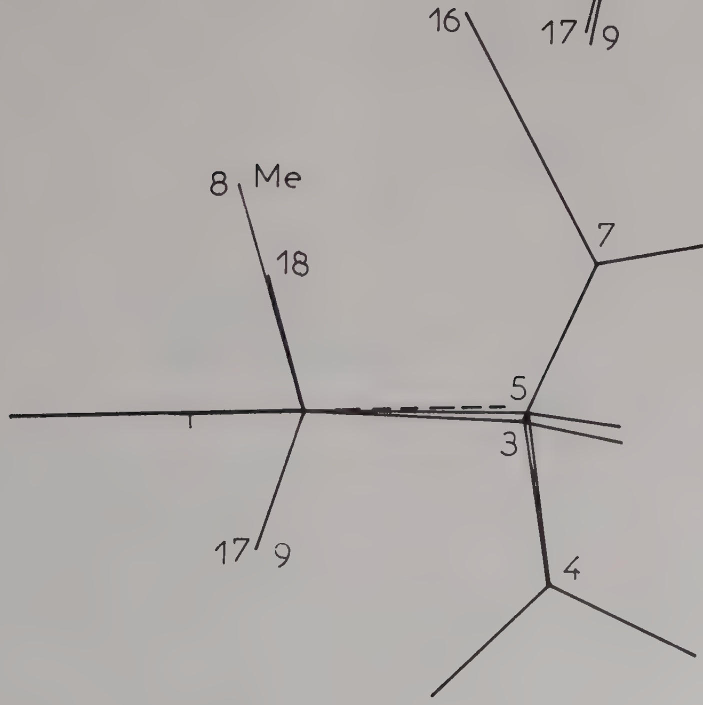


Figure 148

83,623 kcal.

triméthyl - 2,6,6 bicyclo [3.1.1] heptanone - 3

(149-150) triméthyl- 2,6,6 bicyclo [3.1.1] heptanone - 3

Figure 149
83,648 kcal.

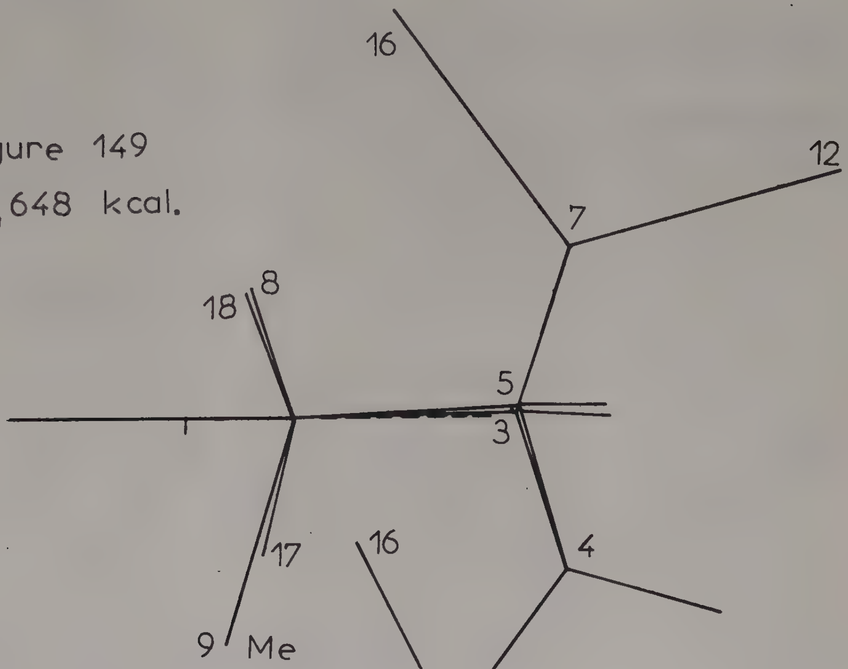


Figure 150
86,180 kcal.

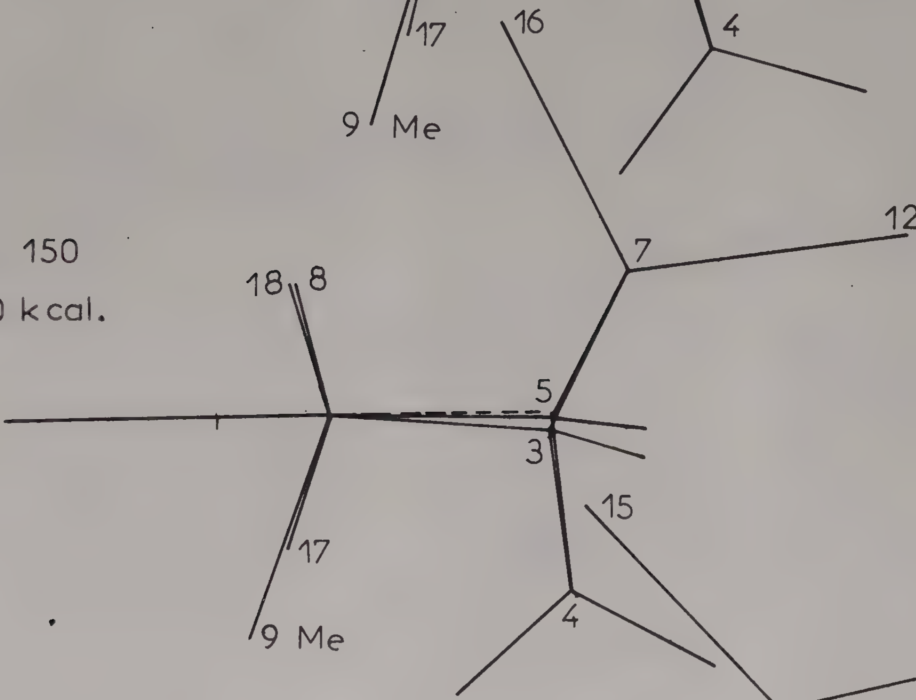
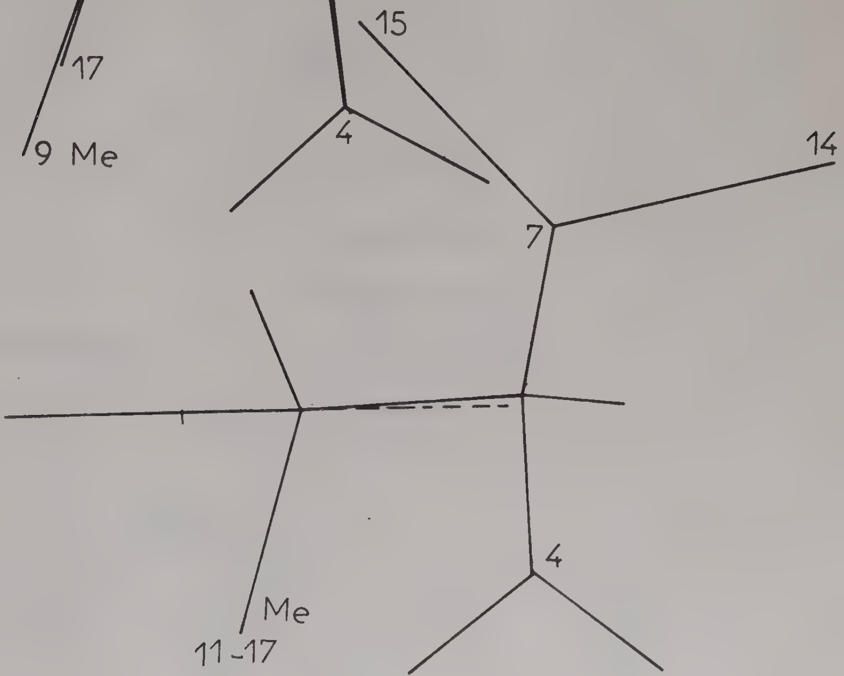
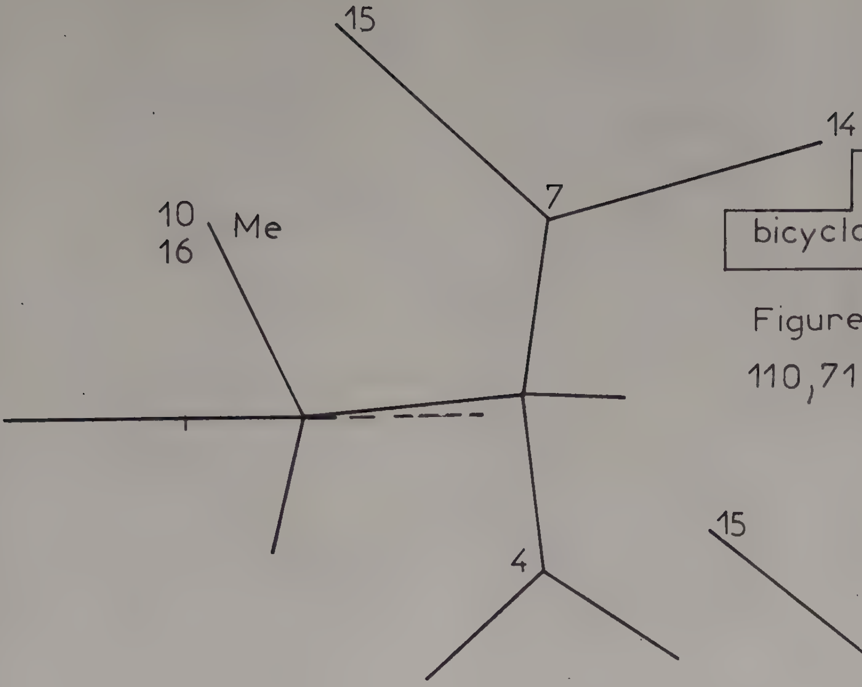


Figure 151
116,737 kcal.

tétraméthyl-2,4,6,6
bicyclo [3.1.1]
heptanone -3





tétraméthyl-2,4,6,6
bicyclo [3.1.1] heptanone-3

Figure 152

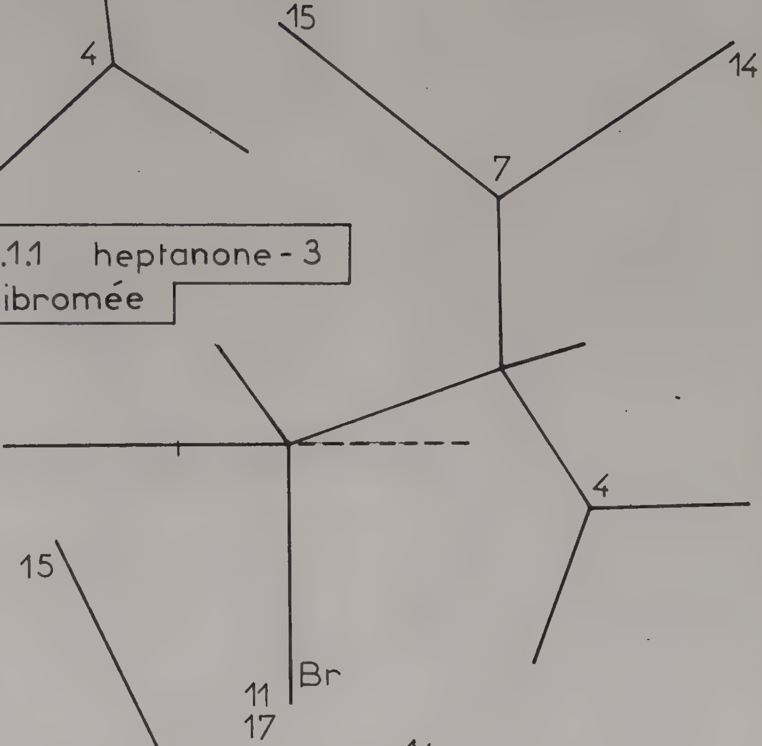
110,719 kcal.

dimethyl-6,6 bicyclo 3.1.1 heptanone-3
αα' dibromée

Figure 153

96,516 kcal.

(93,496 kcal)



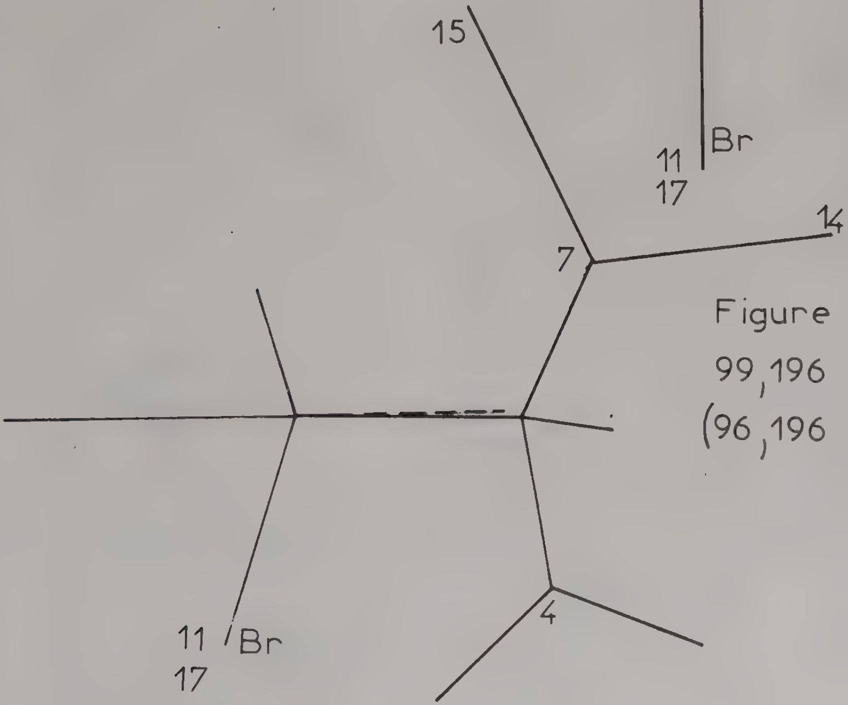


Figure 154

99,196 kcal.

(96,196 kcal)

diméthyl-6,6 bicyclo [3,1,1]
heptanone-3, dibromée

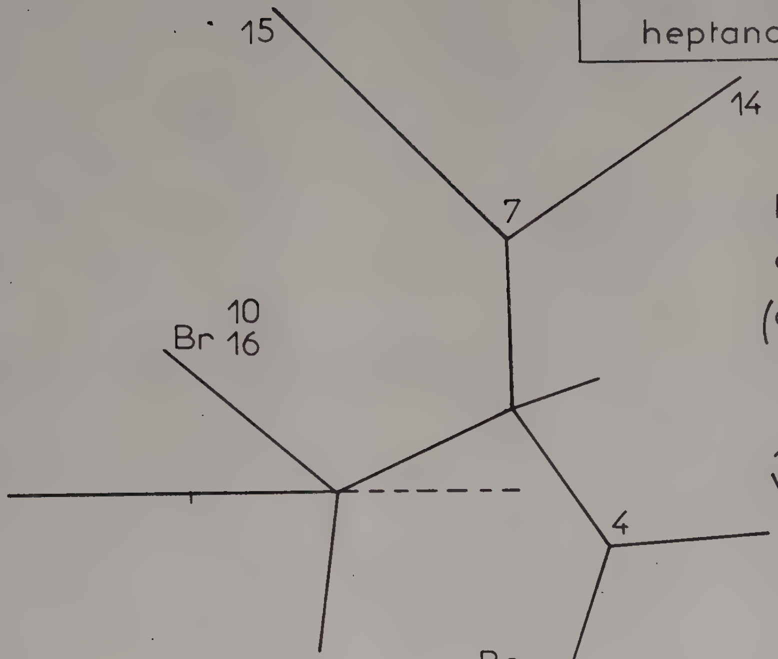


Figure 155
92,002 kcal.
(90,763 kcal)

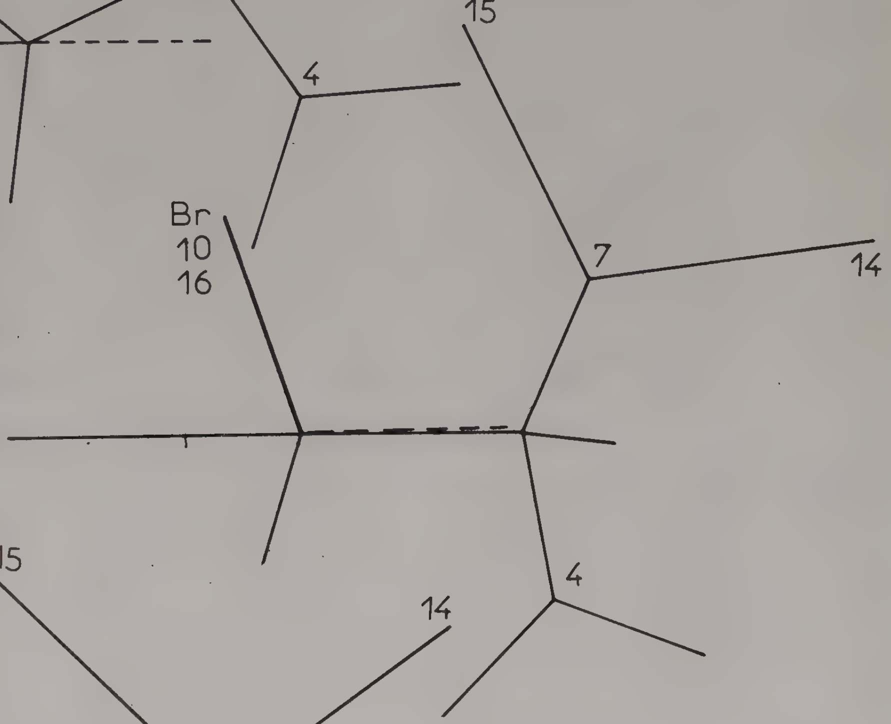


Figure 156
94,402 kcal.
(93,280 kcal)

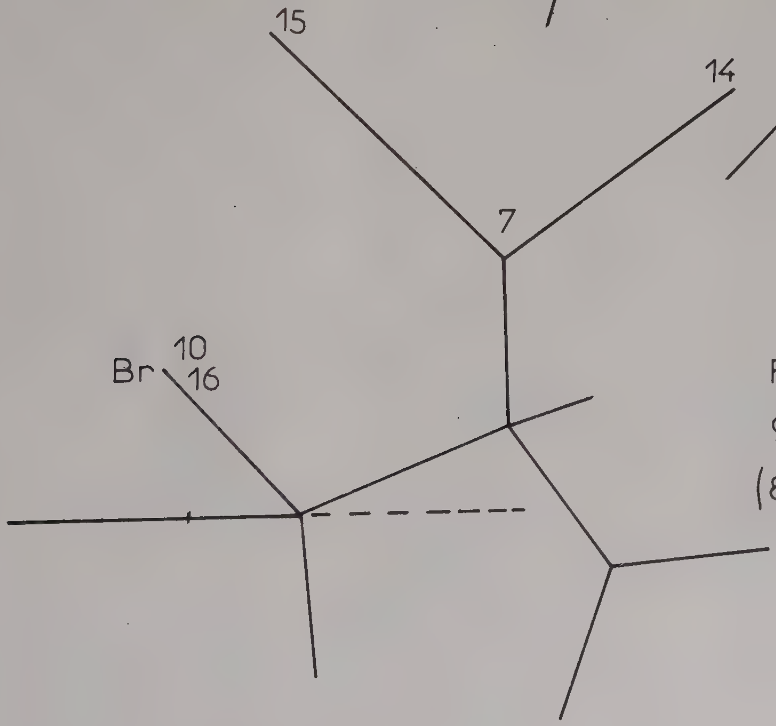


Figure 157
90,507 kcal.
(89,271 kcal)

dimethyl- 6,6 bicyclo [3,1,1] heptanone-3 dibromée

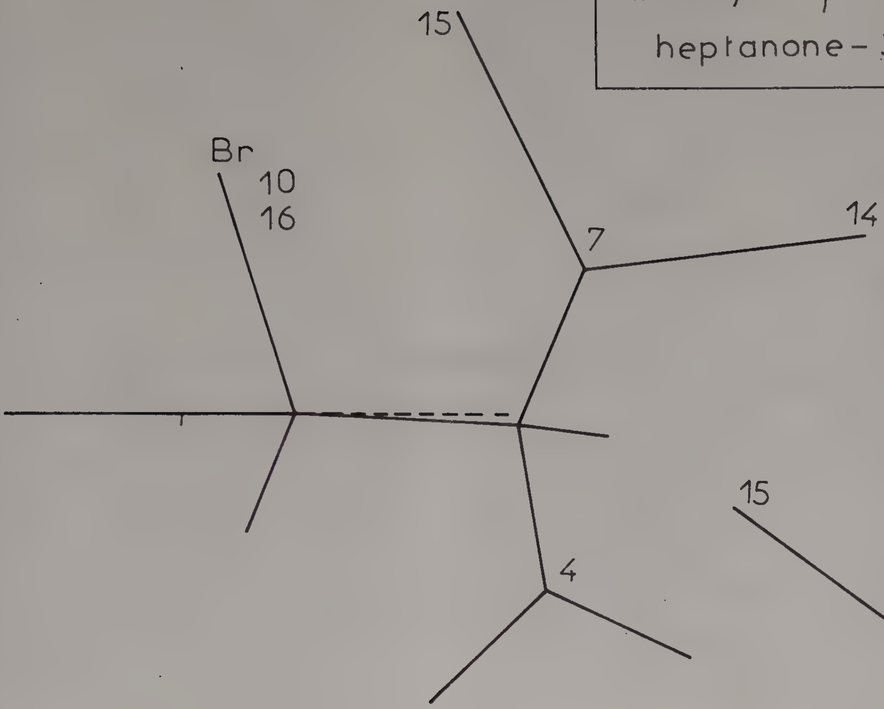


Figure 158
95,168 kcal.
(94,139 kcal)

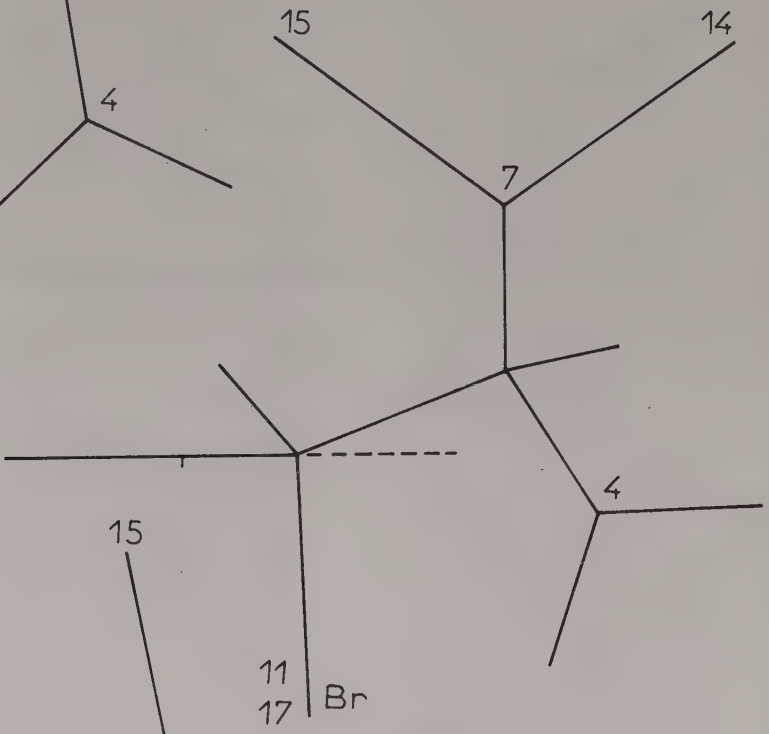


Figure 159
95,705 kcal.
(92,371 kcal)

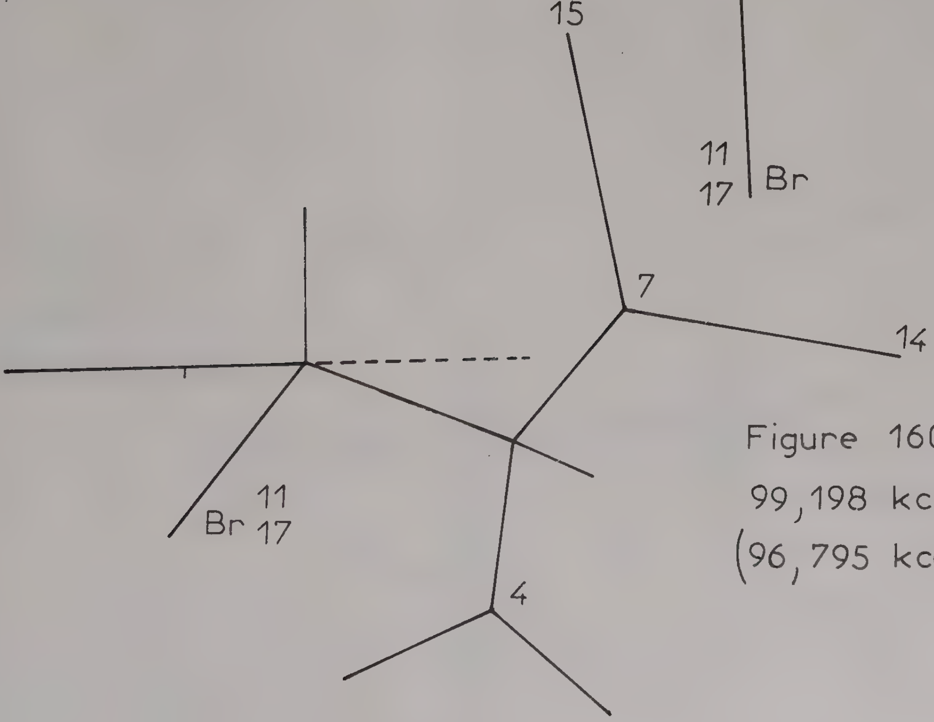


Figure 160
99,198 kcal.
(96,795 kcal)

diméthyl-6,6 bicyclo [3,1,1] heptanone-3, bromée

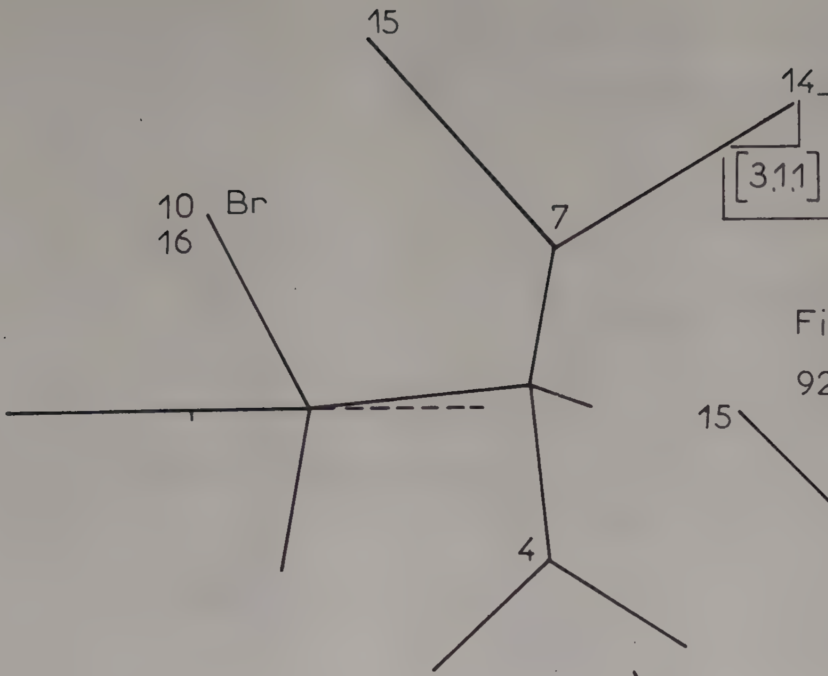


Figure 161
92,219 kcal.

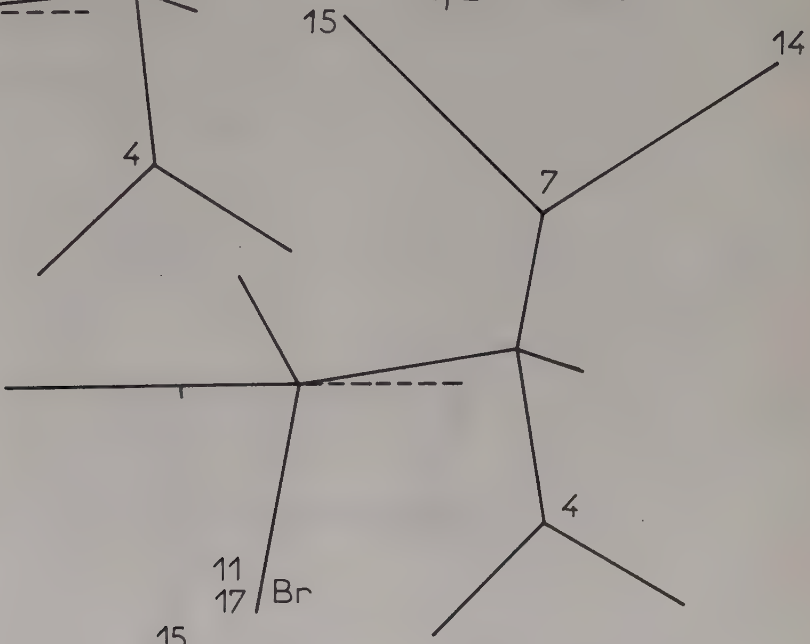


Figure 162
95,269 kcal.

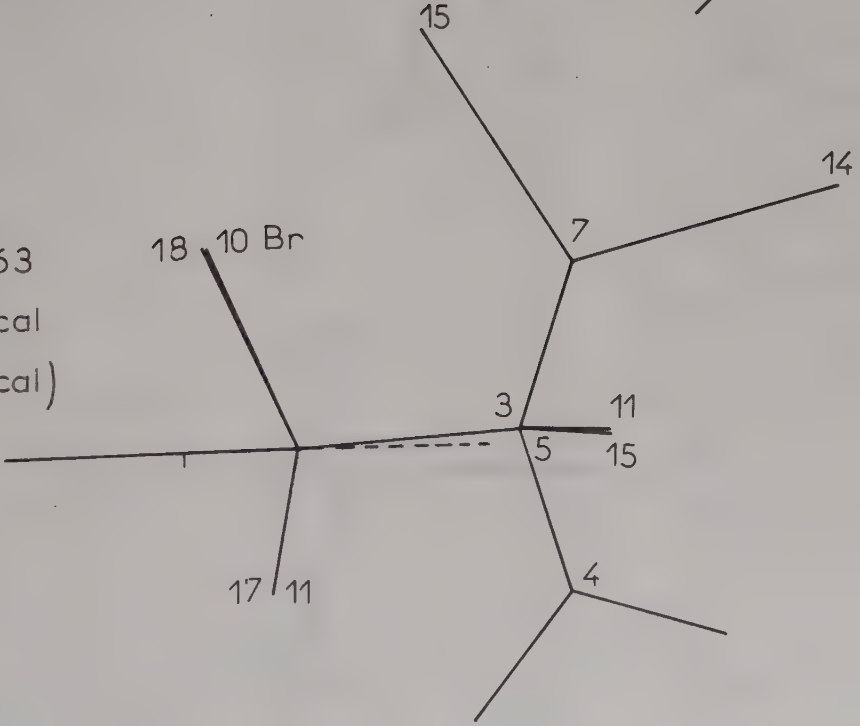


Figure 163
90,737 kcal
(89,658 kcal)

diméthyl-6,6 bicyclo [3.1.1] heptanone-3 bromée

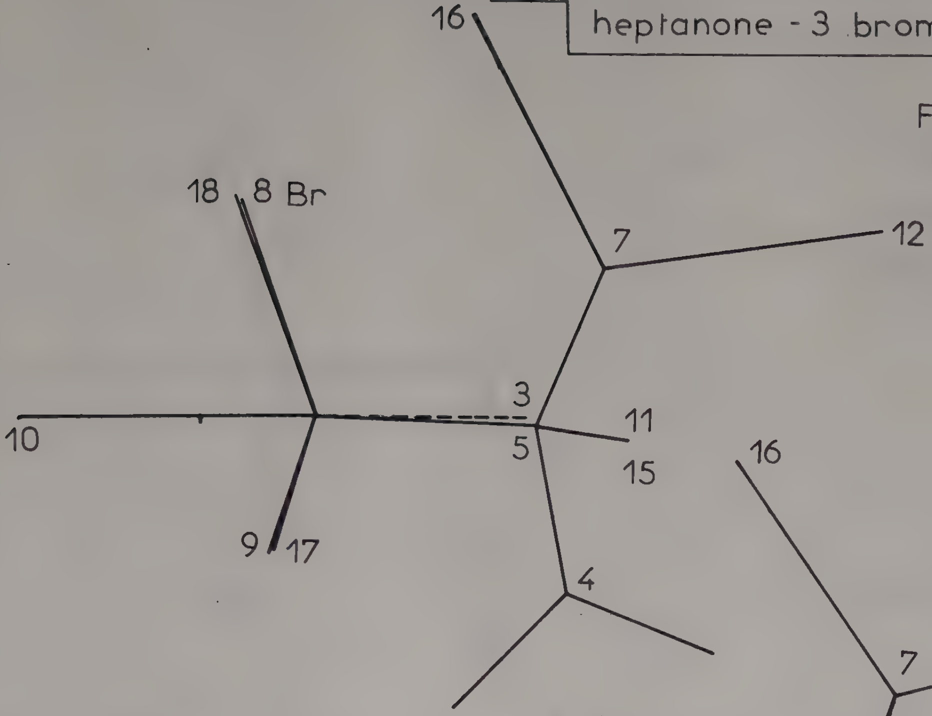


Figure 164
91,385 kcal.
(90,356 kcal)

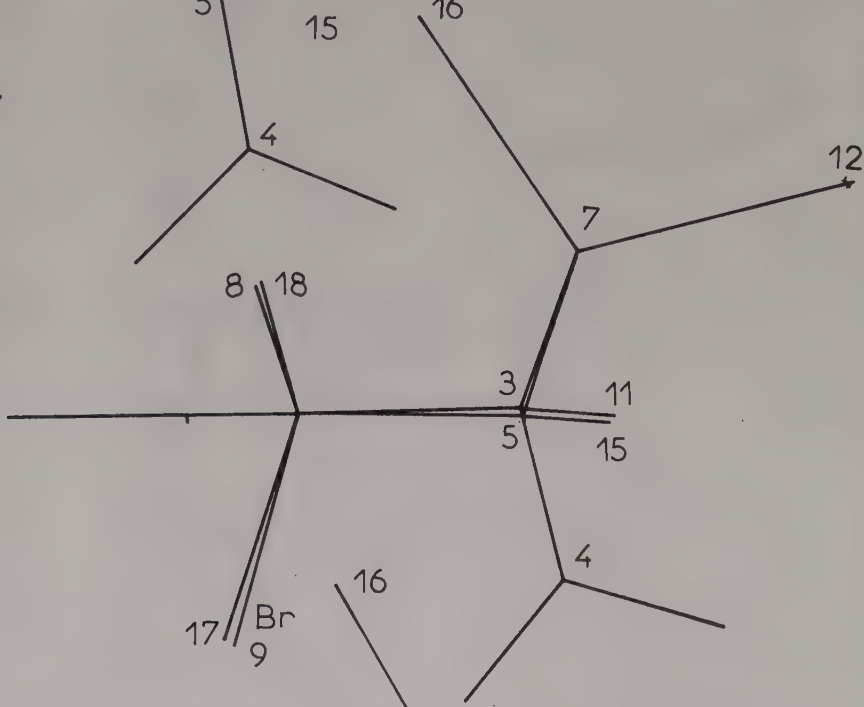


Figure 165
87,566 kcal.
(84,961 kcal)

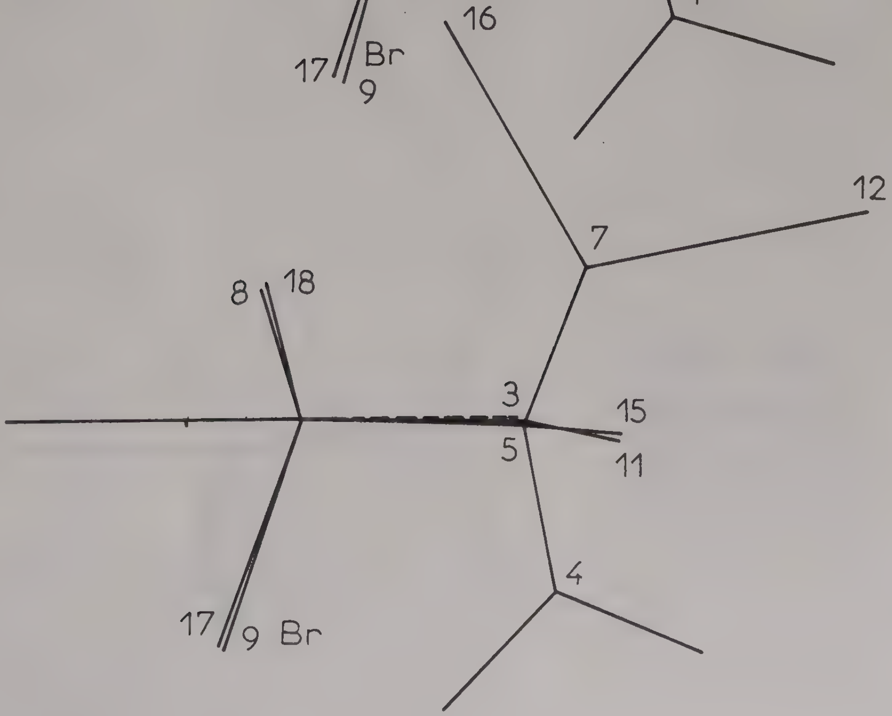


Figure 166
87,802 kcal.
(85,110 kcal)

dimethyl-6,6 bicyclo [3,1,1] heptanone-3
di bromée

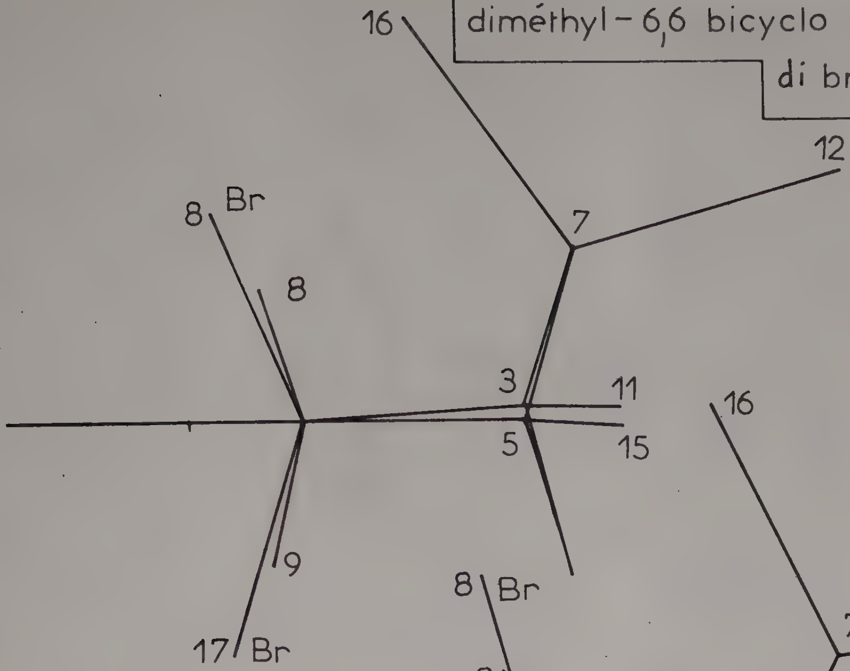


Figure 167
89,274 kcal.
(87,394 kcal)

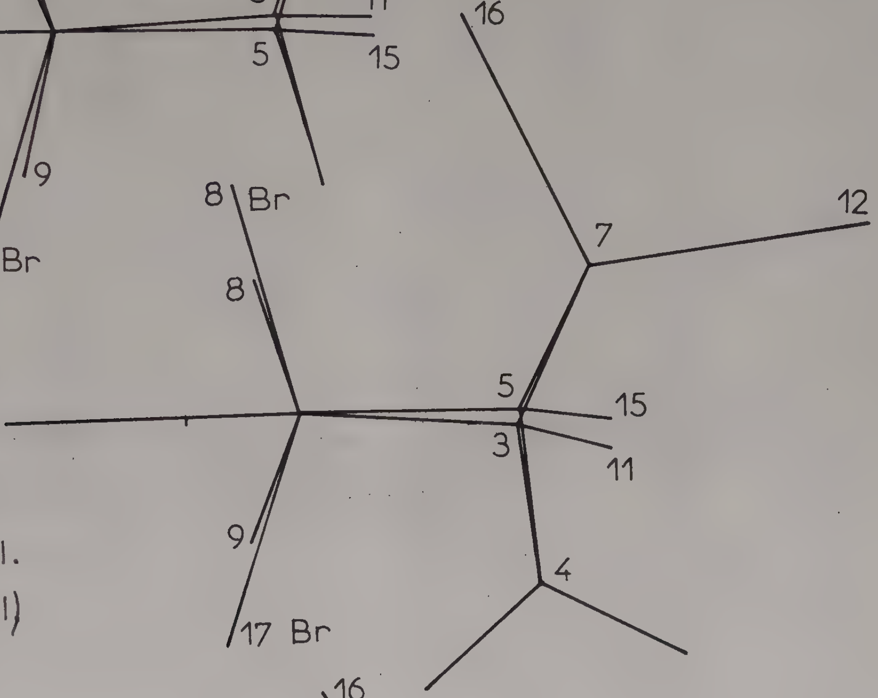


Figure 168
92,847 kcal.
(90,483 kcal)

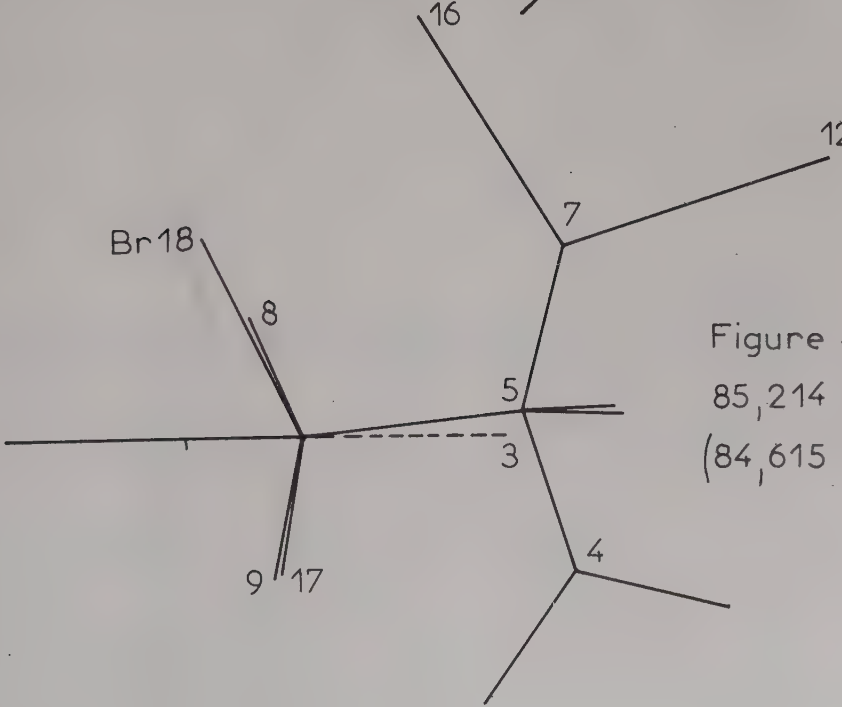


Figure 169
85,214 kcal.
(84,615 kcal)

dimèthyl-6,6 bicyclo [3,1,1] heptanone-3 bromée

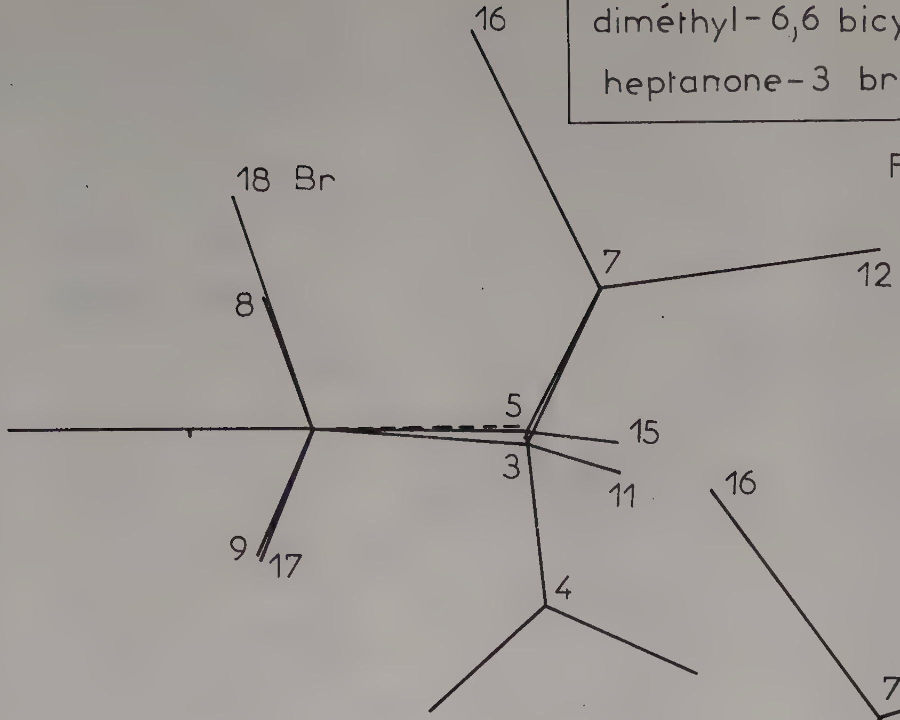


Figure 170
87,397 kcal.
(86,788 kcal)

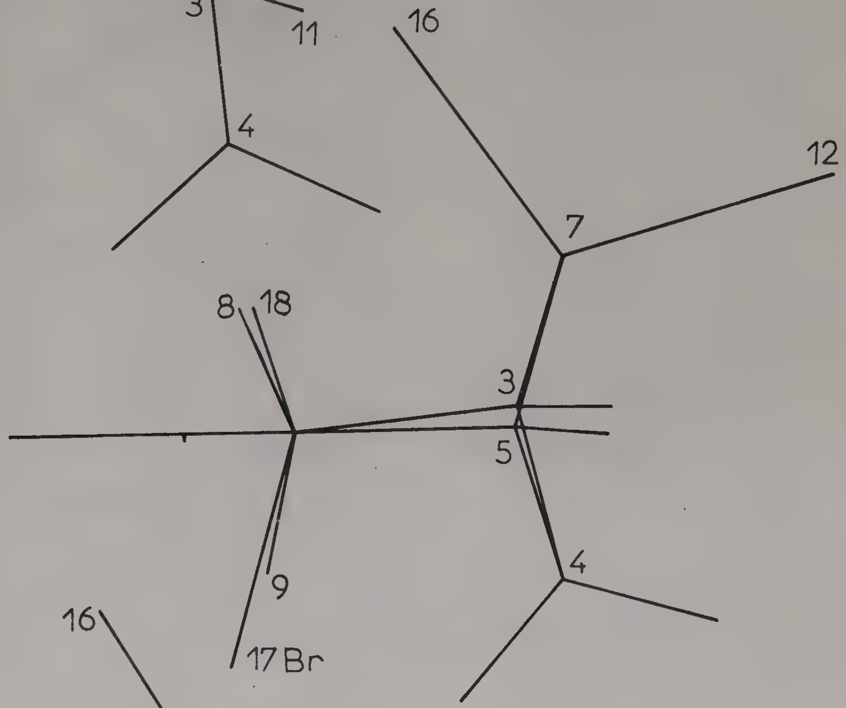


Figure 171
84 364 kcal.
(83,040 kcal)

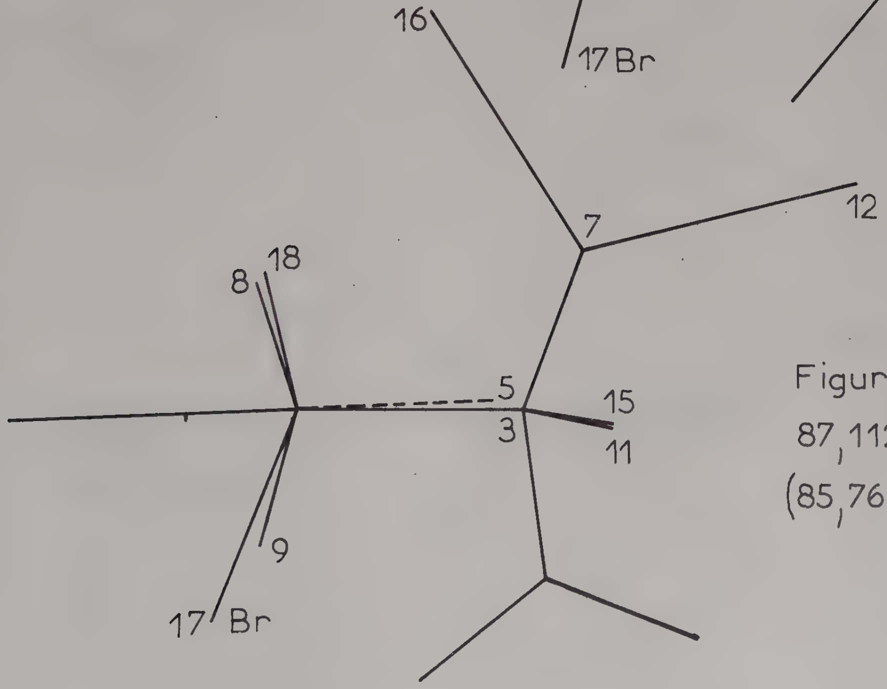


Figure 172
87,112 k cal.
(85,762 k cal)

diméthyl-6,6 bicyclo [3,1,1] heptanol -3

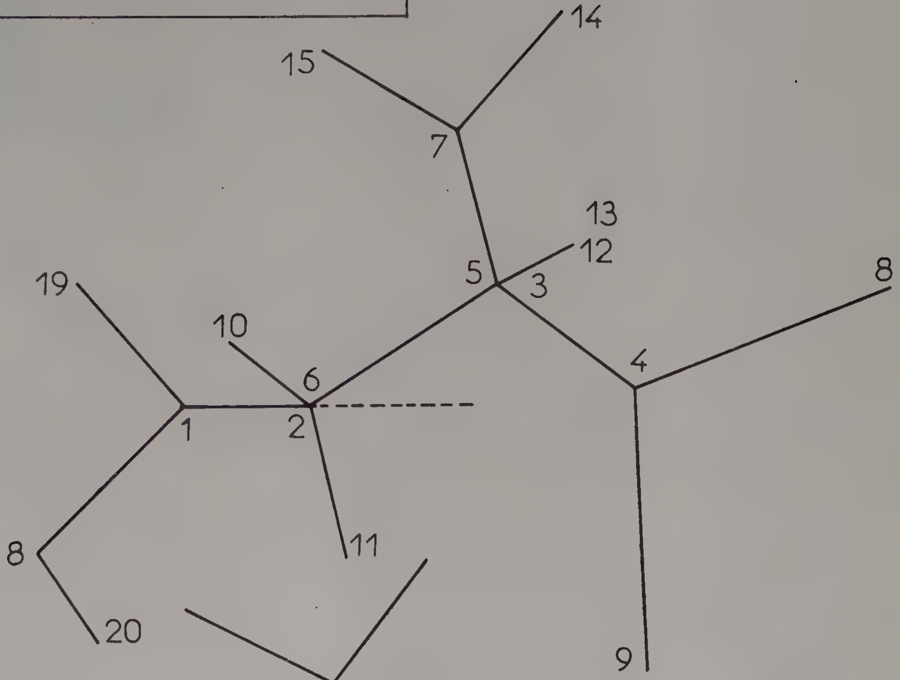


Figure 173
94,994 kcal.

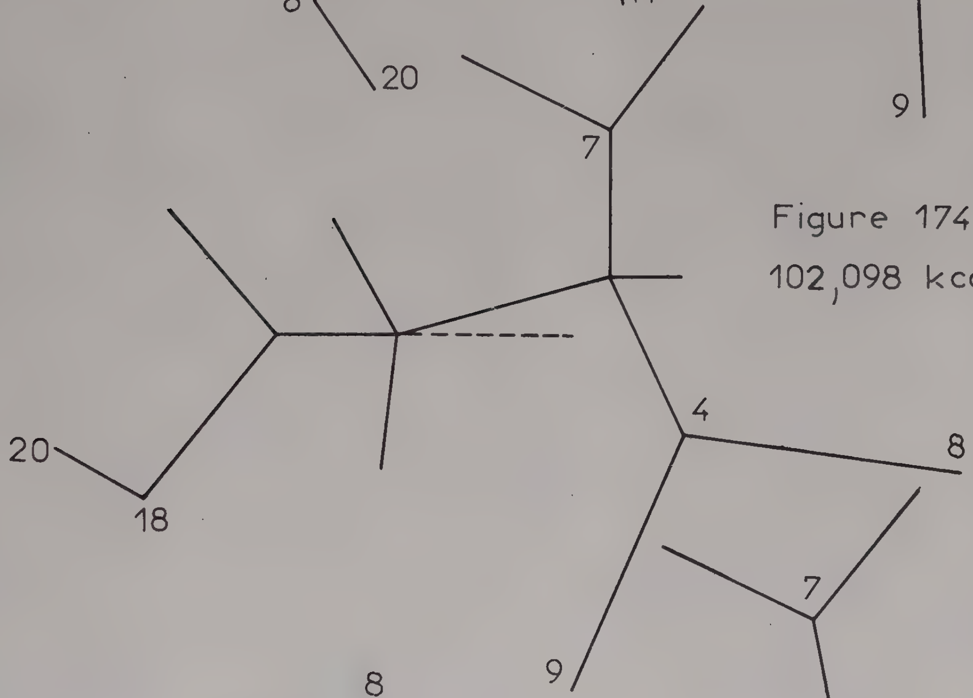


Figure 174
102,098 kcal.

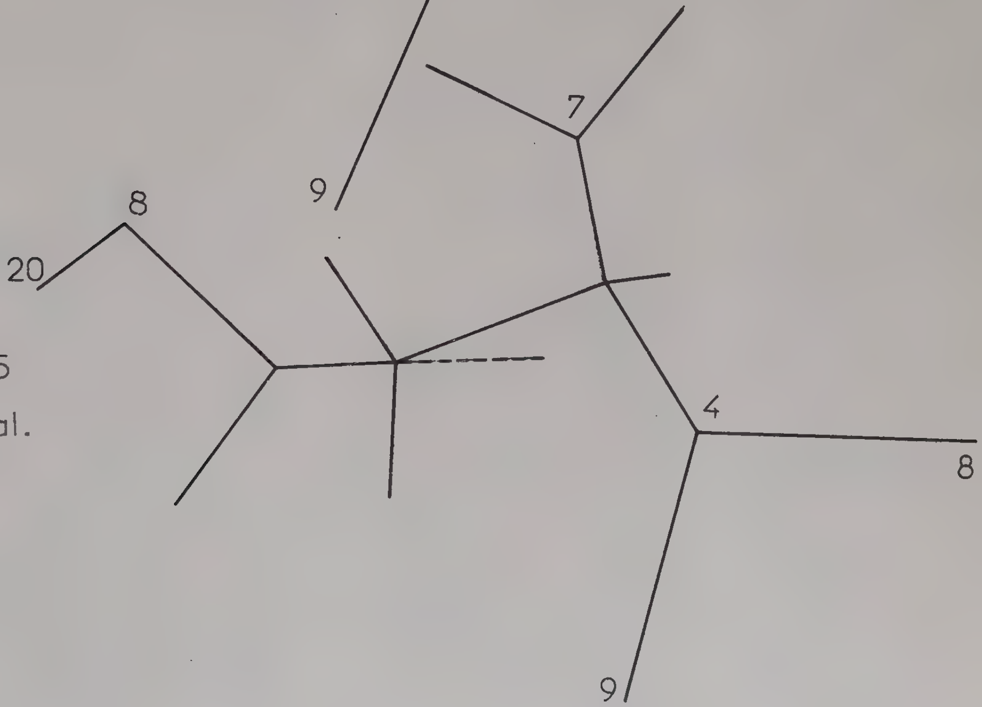


Figure 175
98,274 kcal.

tétraméthyl - 2,4,6,6
bicyclo [3.1.1] heptanol - 3

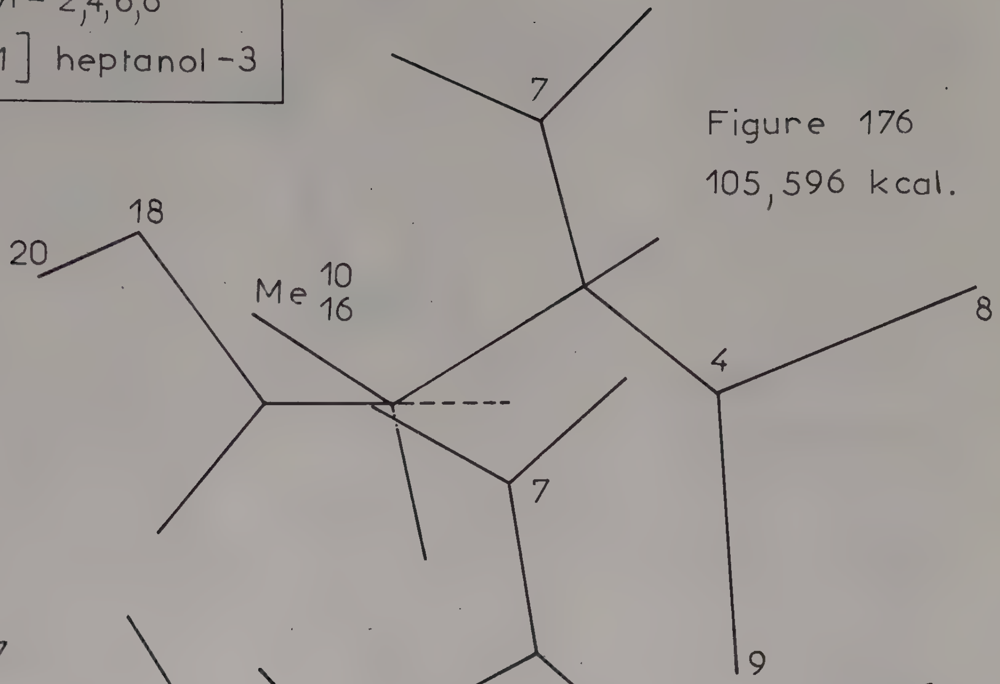


Figure 176
105,596 kcal.

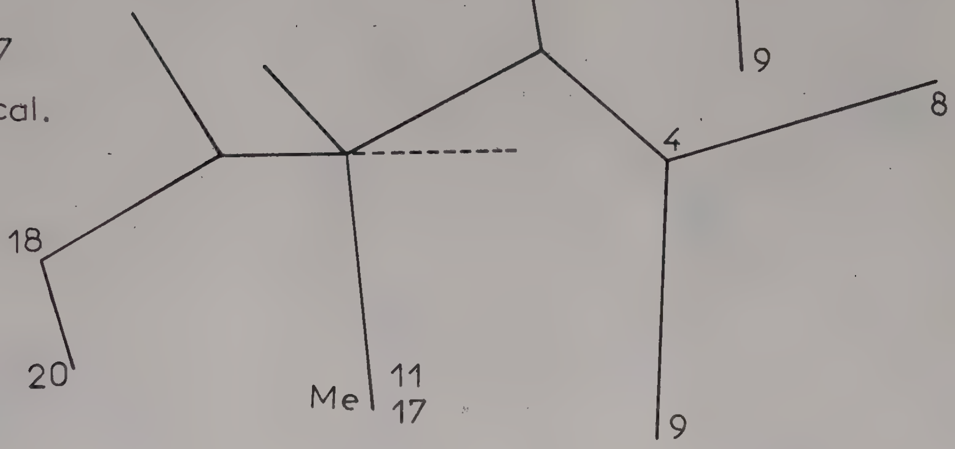


Figure 177
110,040 kcal.

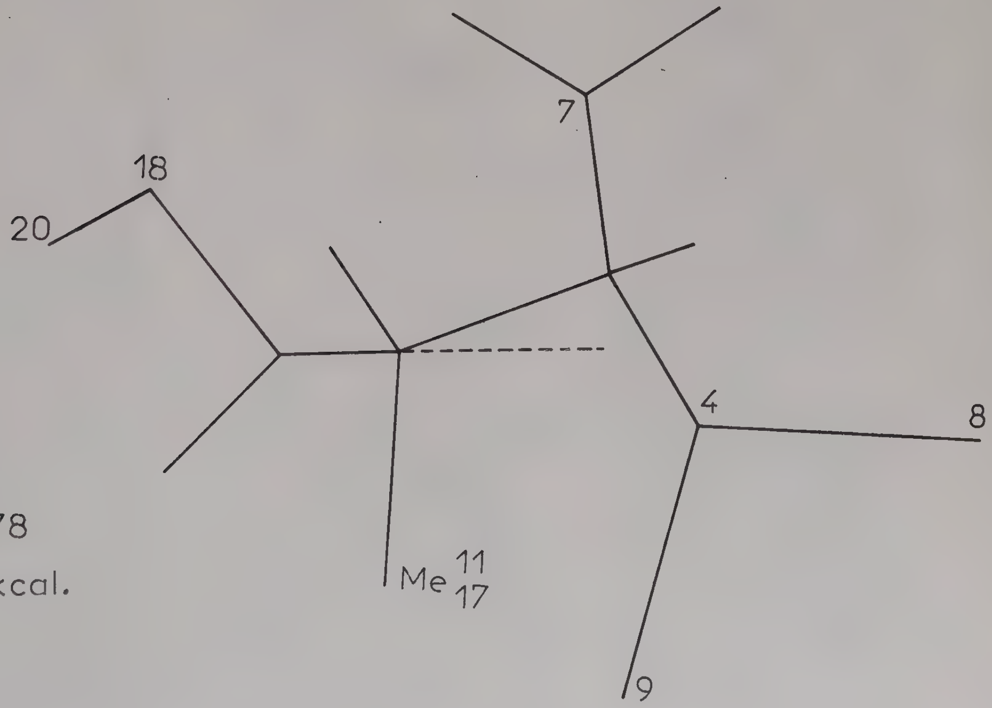


Figure 178
115,821 kcal.

bicyclo [3.2.1] octane

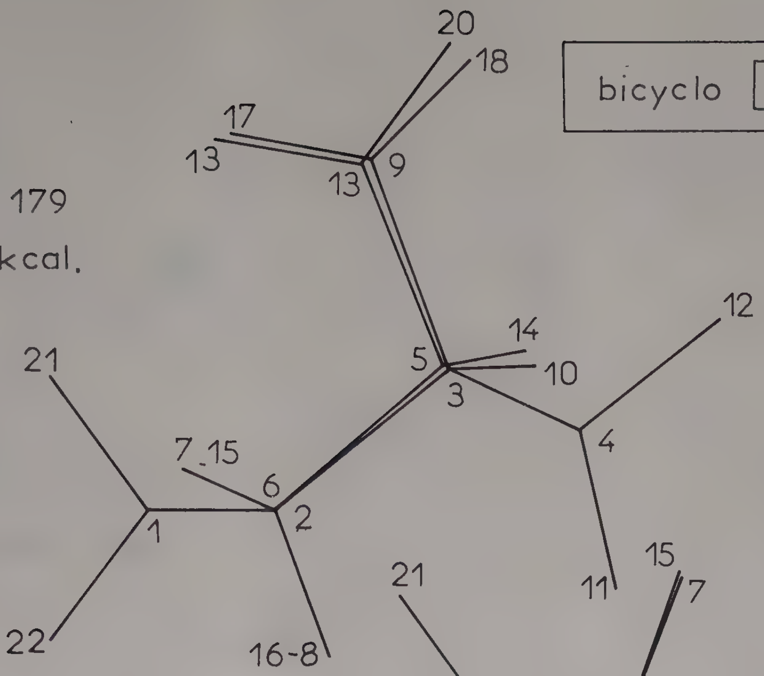


Figure 179
19,456 kcal.

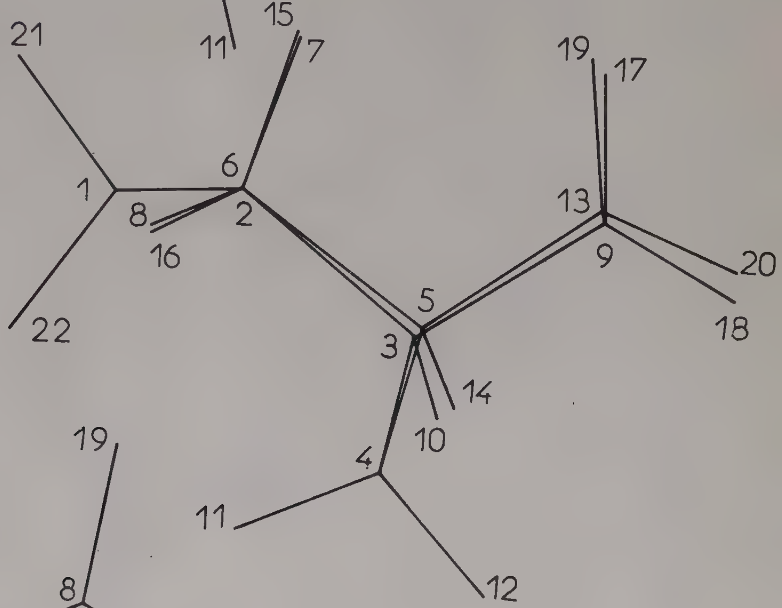


Figure 180
25,665 kcal.

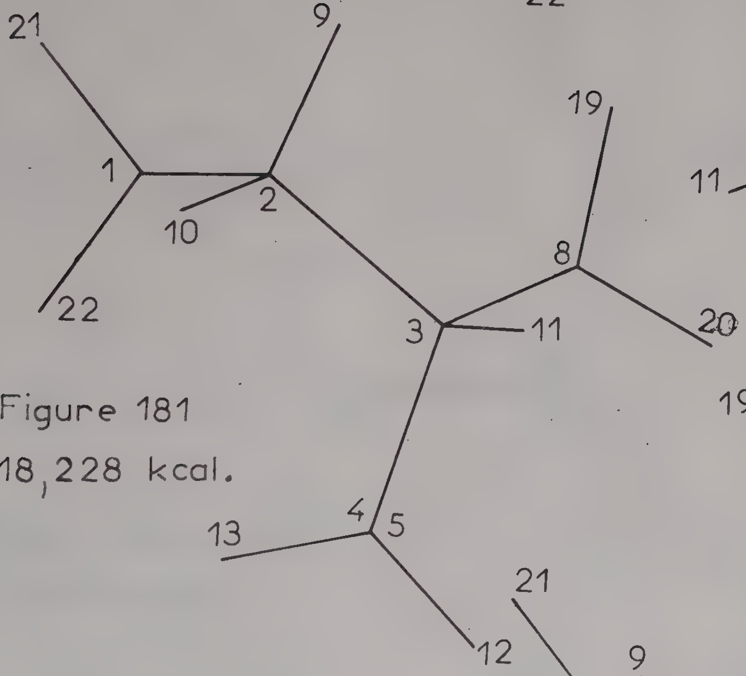


Figure 181
18,228 kcal.

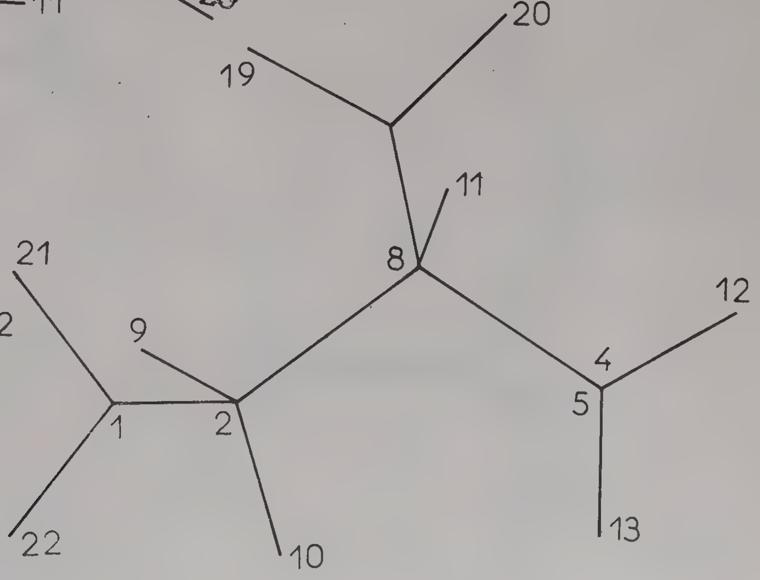


Figure 182
24,083 kcal.

bicyclo [3,2,1] octane

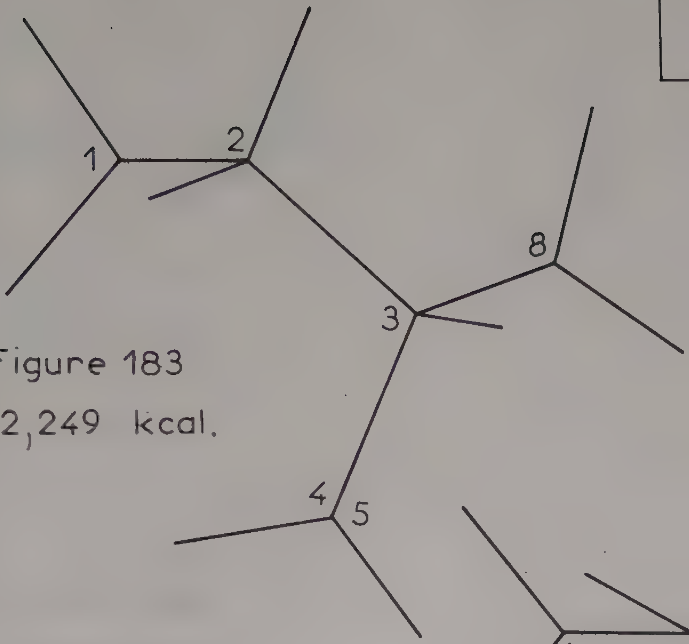


Figure 183
12,249 kcal.

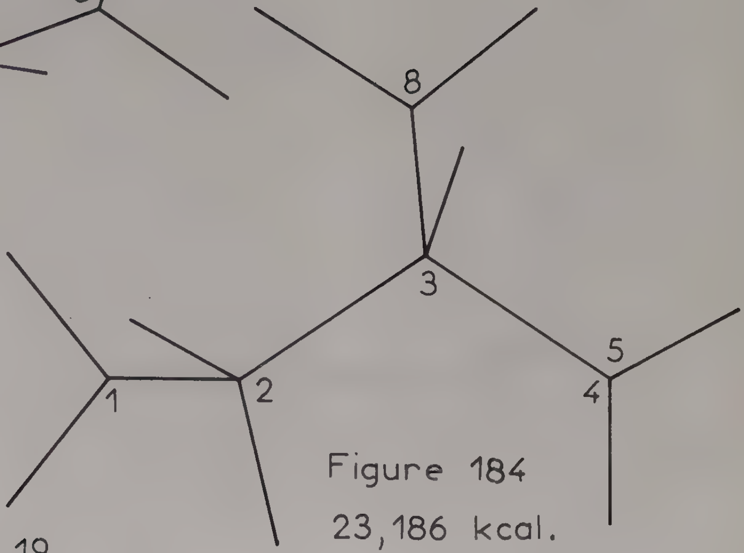


Figure 184
23,186 kcal.

bicyclo [3,2,1] octanone-3

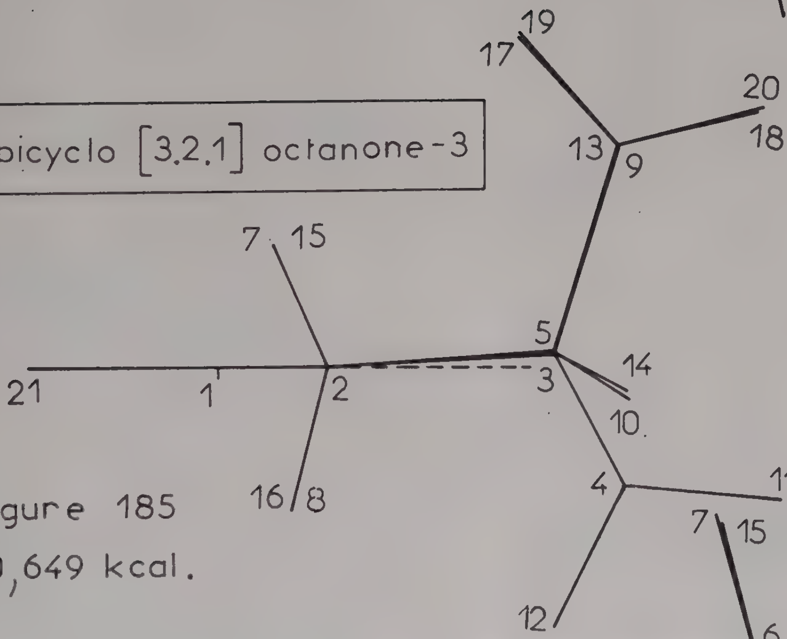


Figure 185
20,649 kcal.

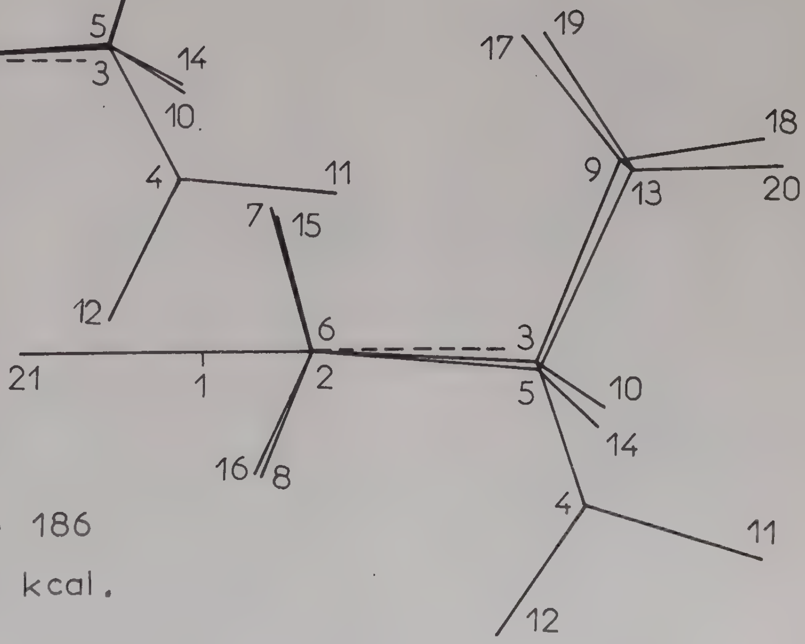


Figure 186
21,404 kcal.

bicyclo [3,2,1] octanone-3

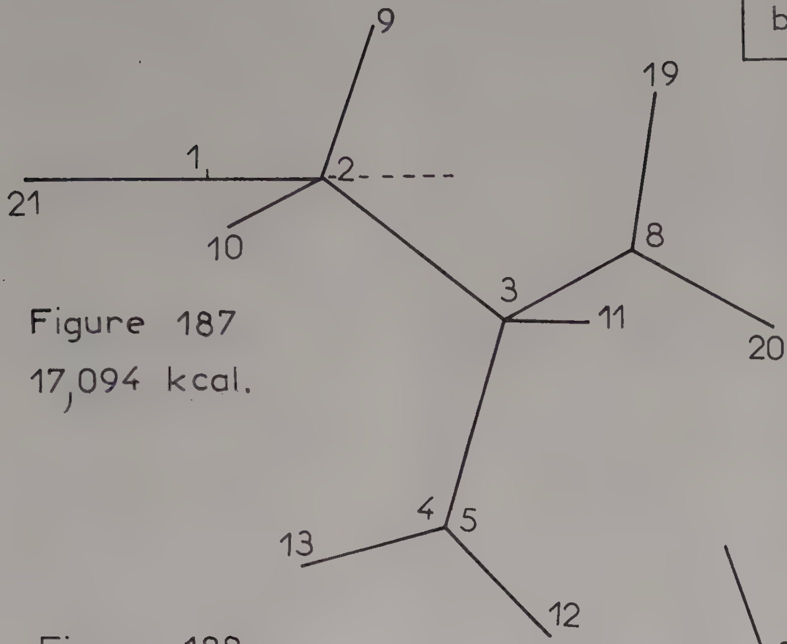


Figure 187
17,094 kcal.

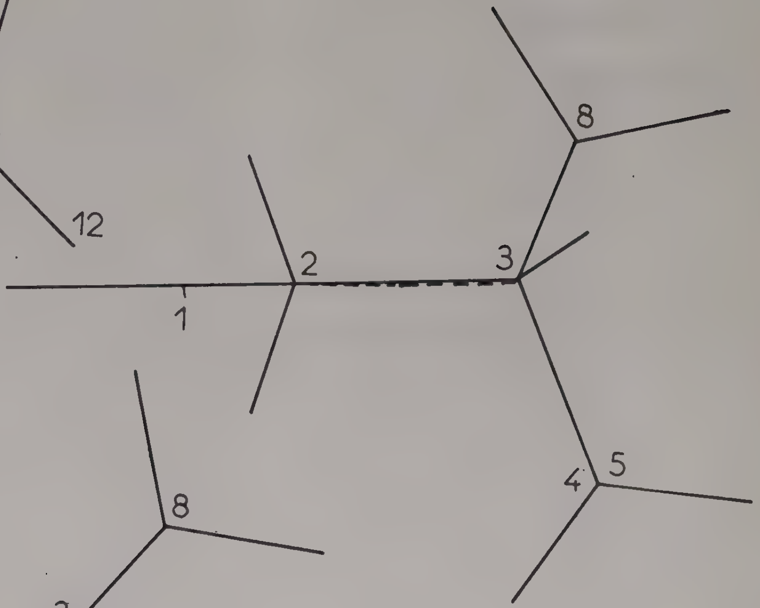


Figure 188
20,693 kcal.

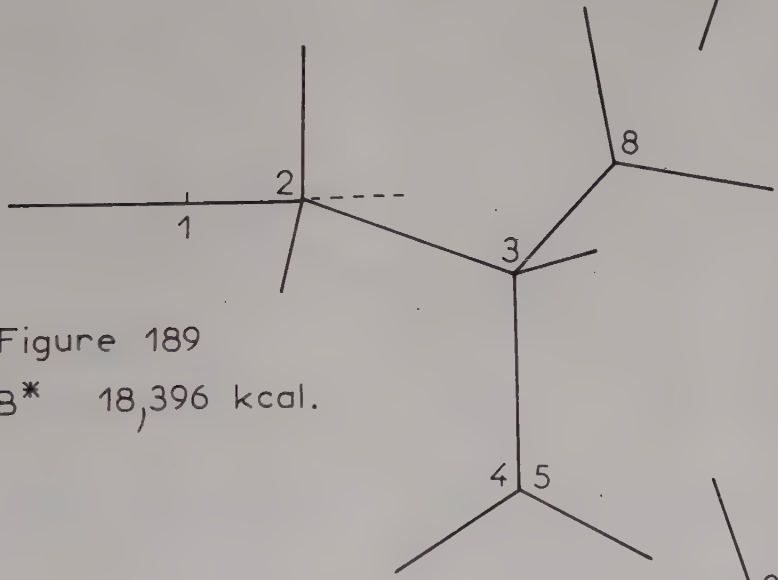
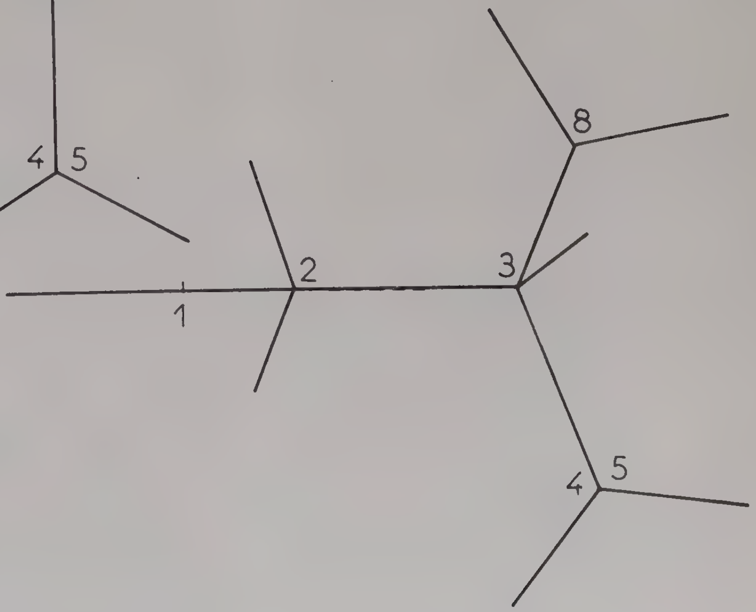


Figure 189
B* 18,396 kcal.



B* Figure 190
19,328 kcal.

bicyclo [3.2.1] octanone - 3

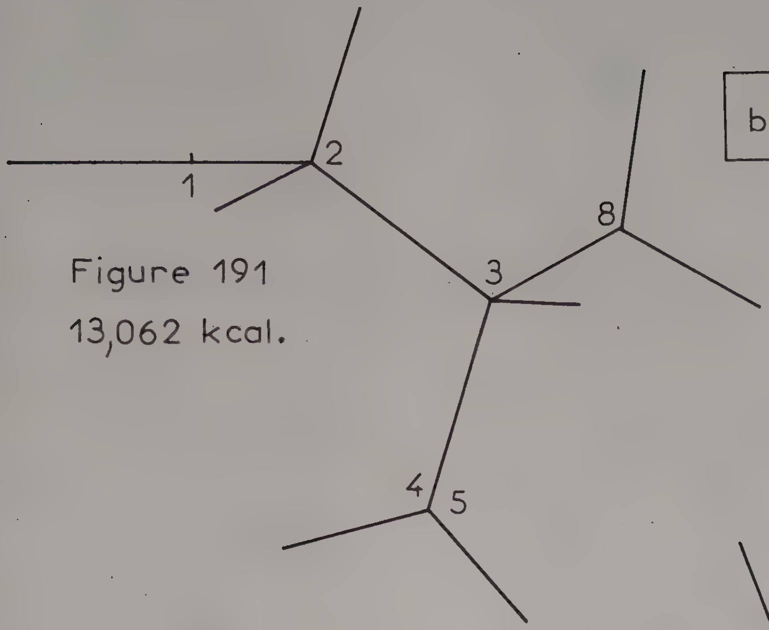


Figure 191
13,062 kcal.

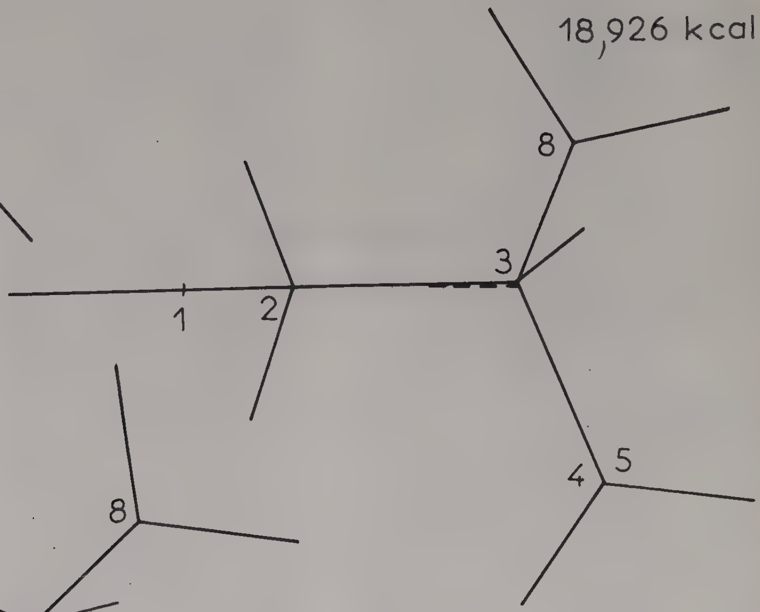


Figure 192
18,926 kcal.

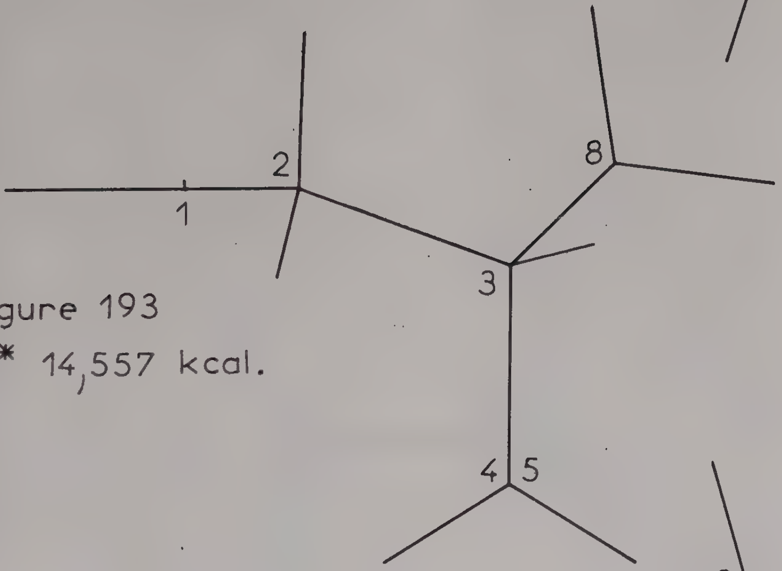
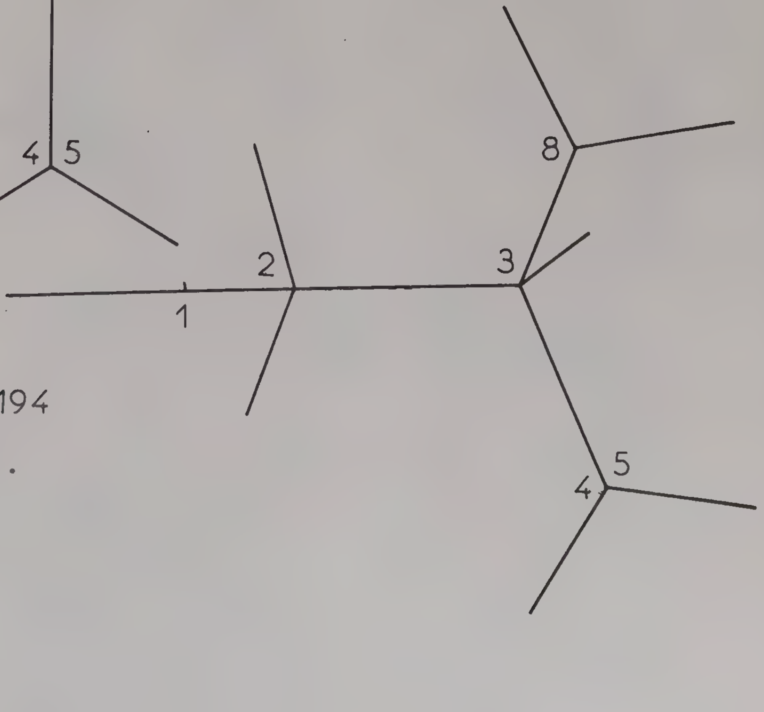


Figure 193
B* 14,557 kcal.



B* Figure 194
17,708 kcal.

bicyclo [3.2.1] octanone-3
α bromée

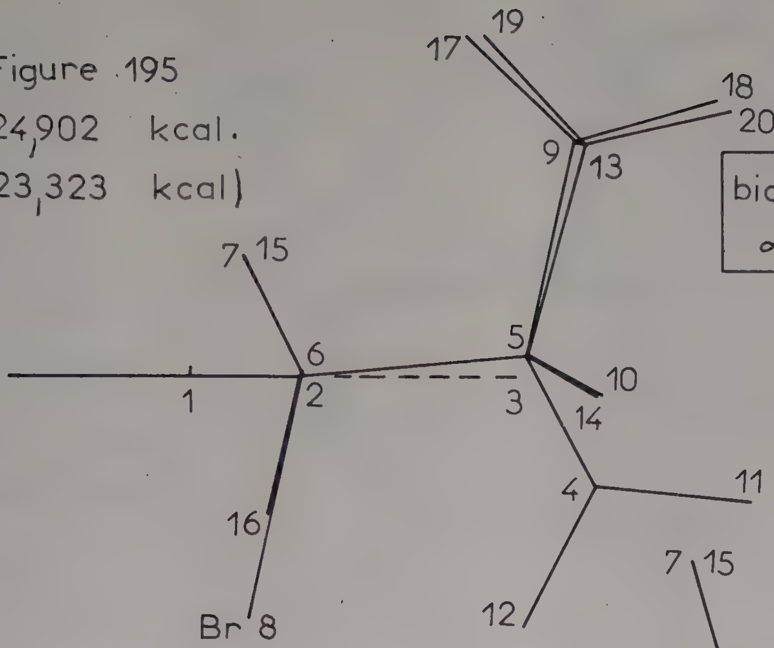


Figure 195
24,902 kcal.
(23,323 kcal)

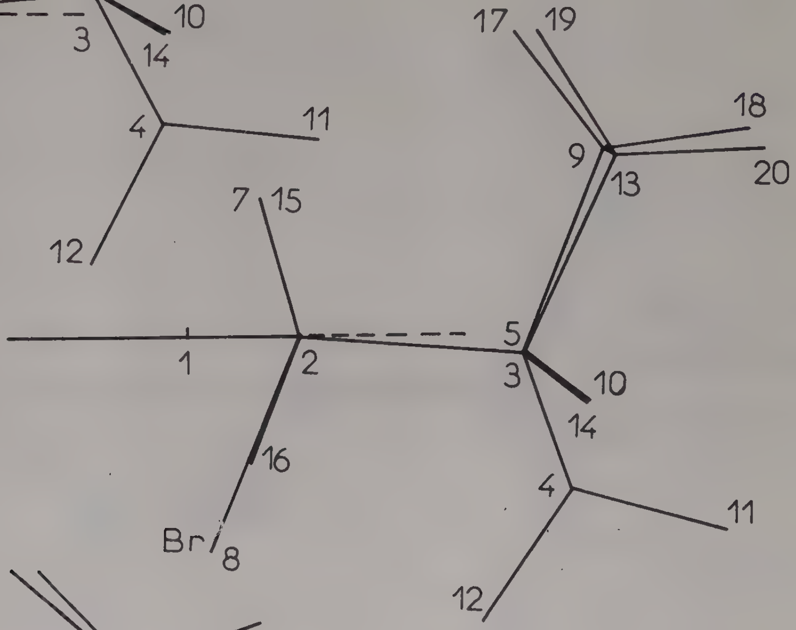


Figure 196
25,955 kcal.
(24,477 kcal)

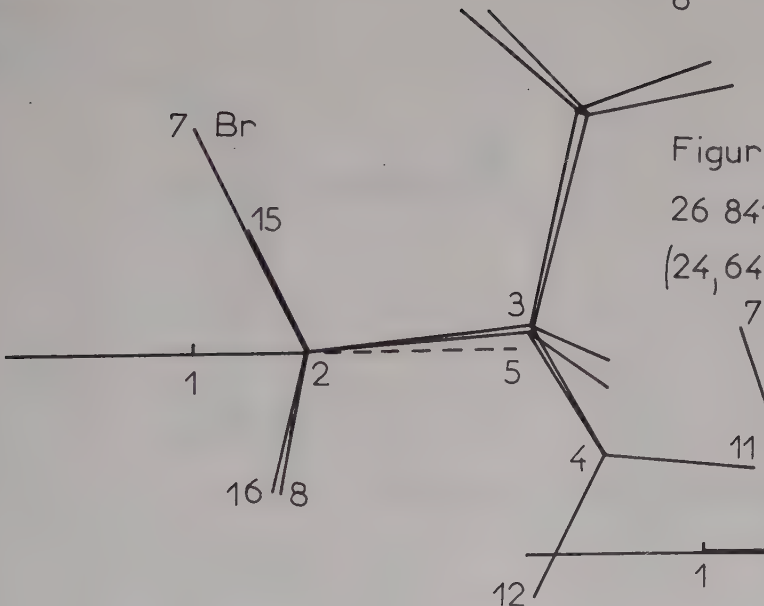


Figure 197
26 841 kcal.
(24,646 kcal)

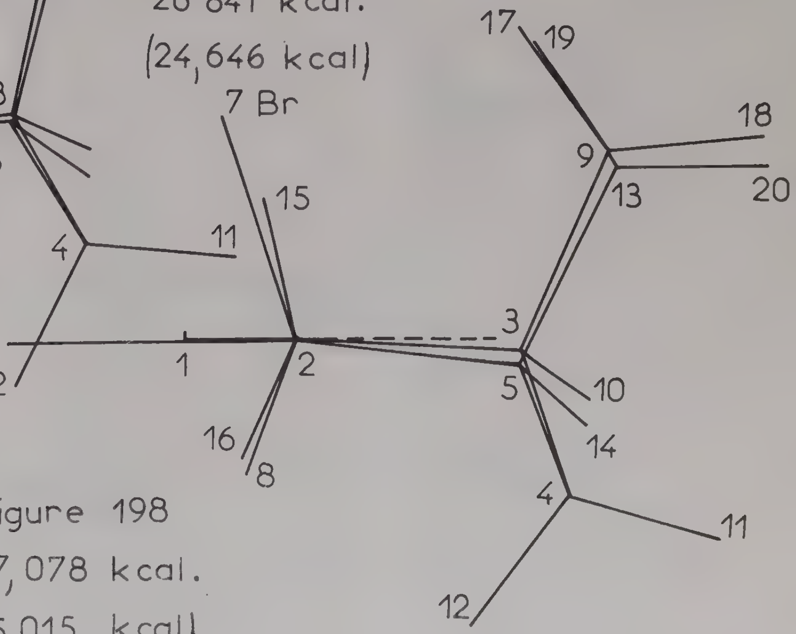


Figure 198
27,078 kcal.
(25,015 kcal)

bicyclo [3.2.1] octanone -3
αα' cis-dibromée

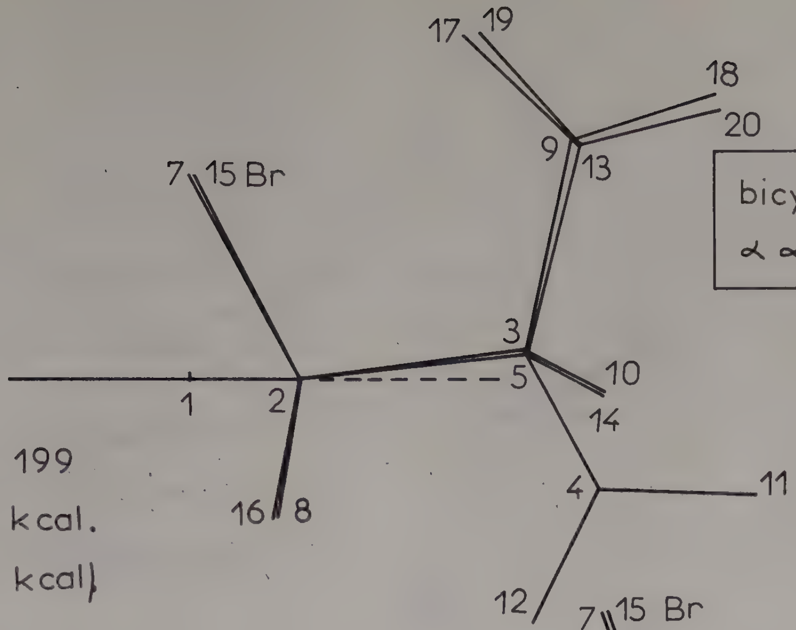


Figure 199
32,591 kcal.
(28,157 kcal)

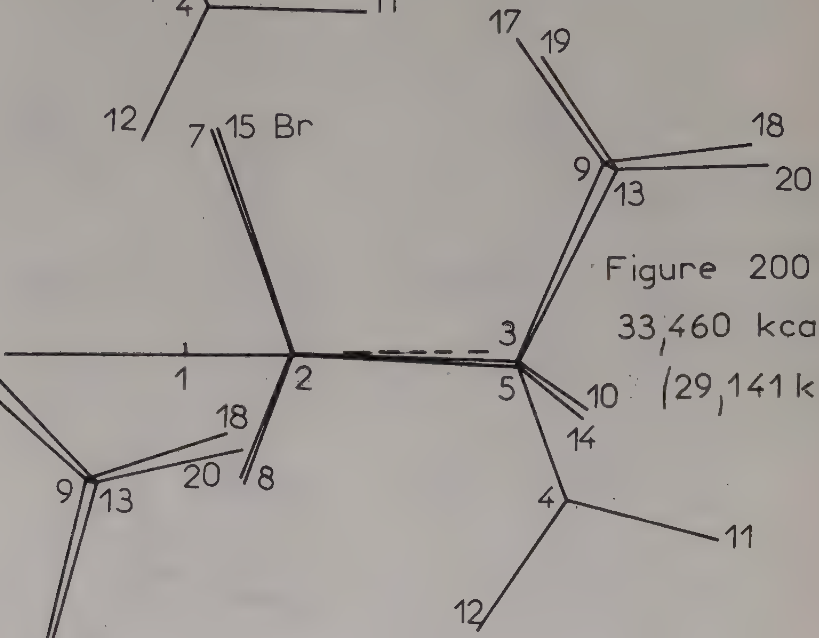


Figure 200
33,460 kcal.
(29,141 kcal)

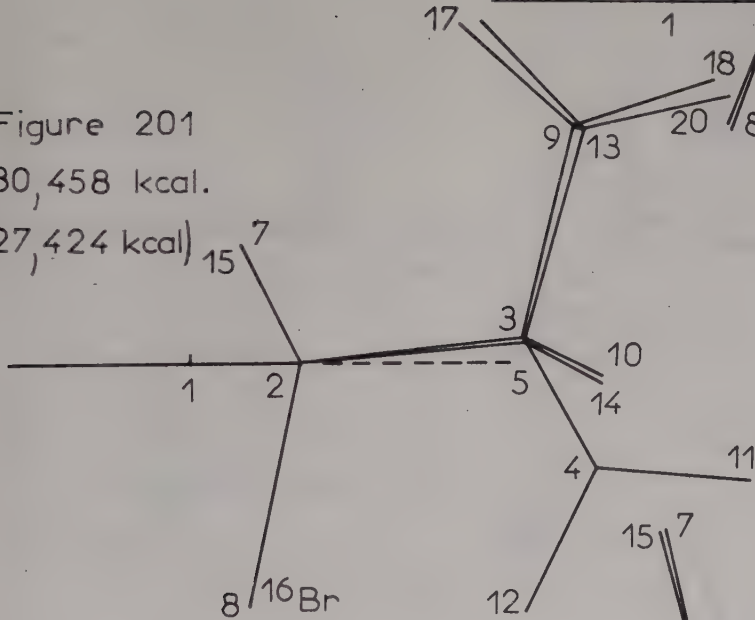


Figure 201
30,458 kcal.
(27,424 kcal)

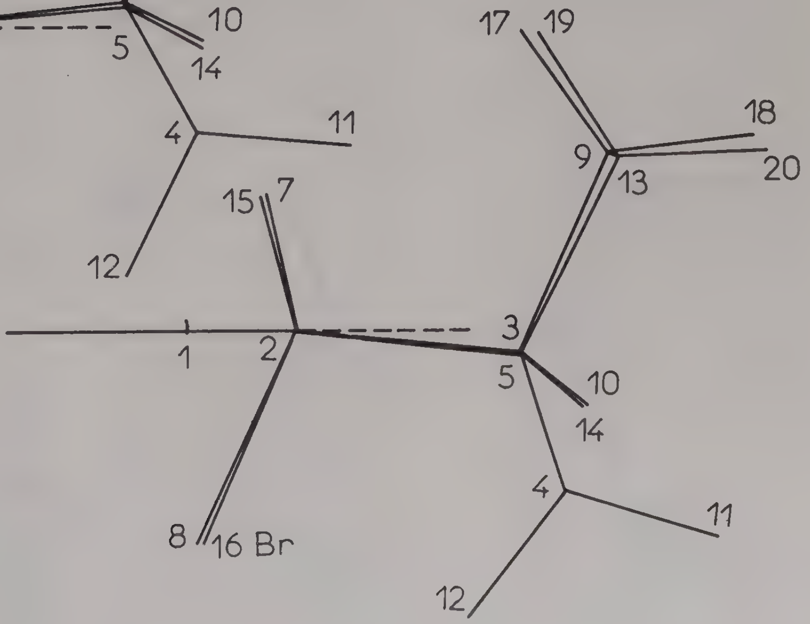


Figure 202
31 594 kcal.
(28,680 kcal)

bicyclo [3.2.1] octanone - 3
αα' cis-dibromée

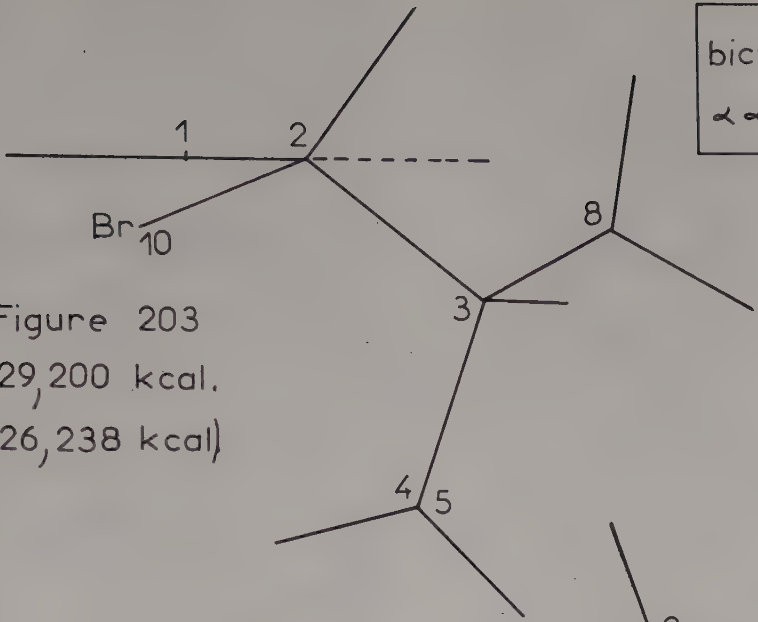


Figure 203
29,200 kcal.
(26,238 kcal)

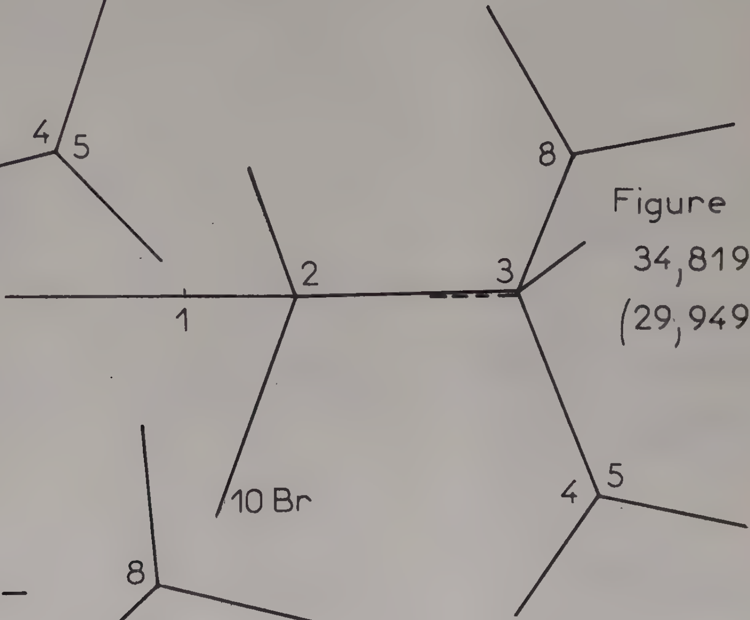


Figure 204
34,819 kcal.
(29,949 kcal)

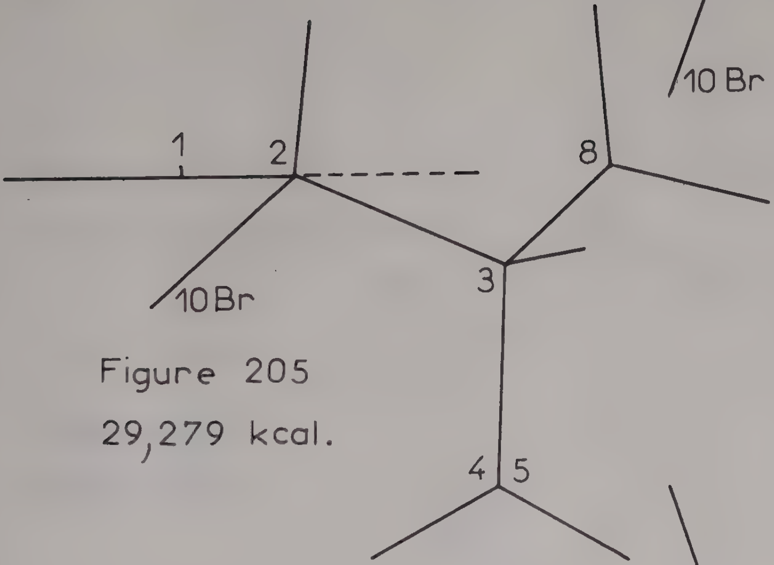


Figure 205
29,279 kcal.

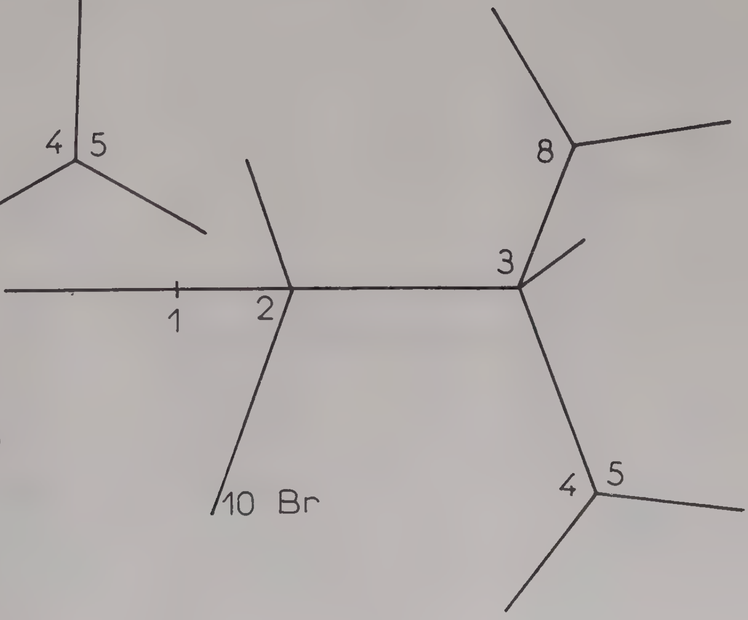


Figure 206
34,030 kcal.

bicyclo [3.2.1] octanone 3
αα'- cis - dibromée

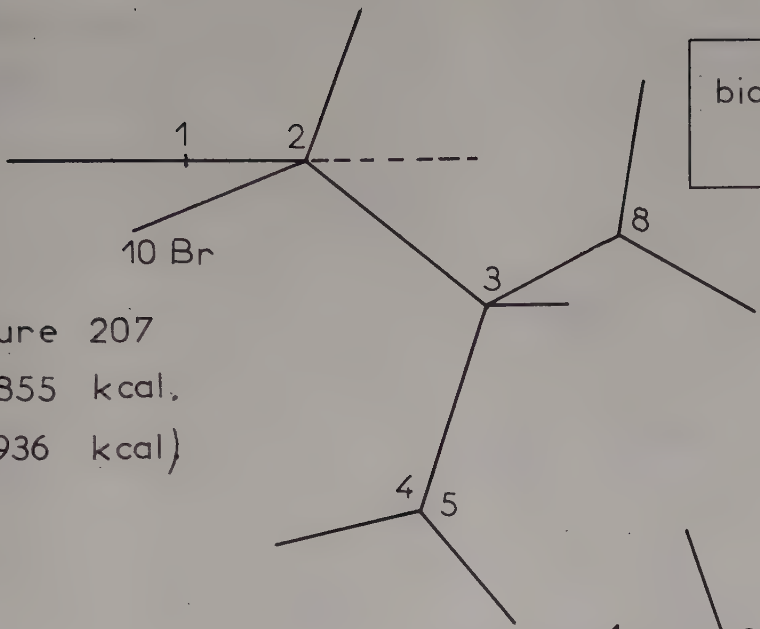


Figure 207
26,855 kcal.
(23,936 kcal)

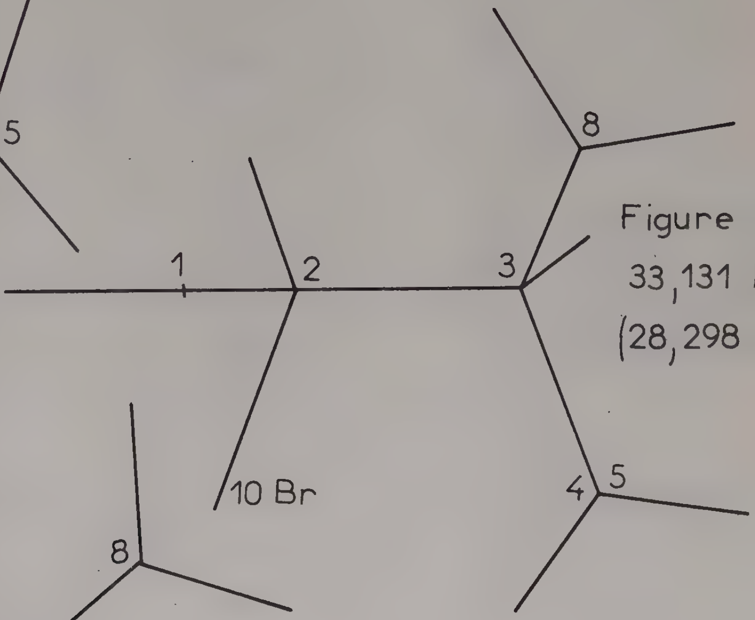


Figure 208
33,131 kcal.
(28,298 kcal)

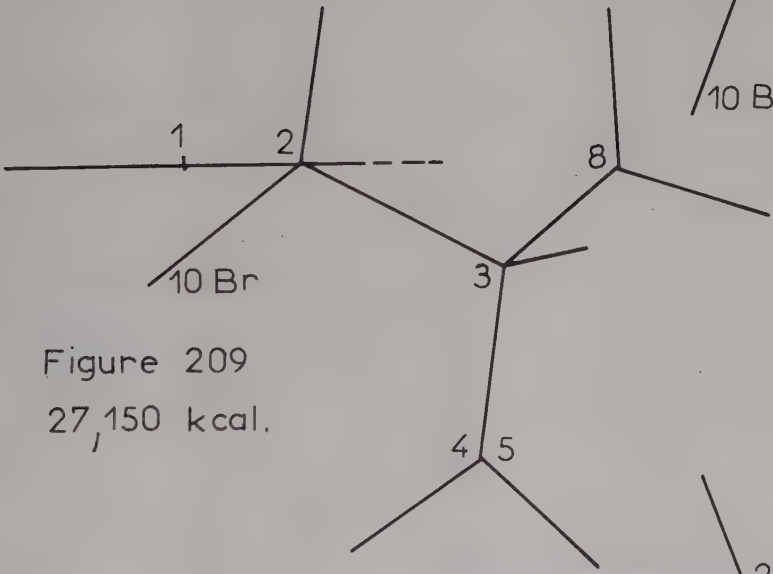


Figure 209
27,150 kcal.

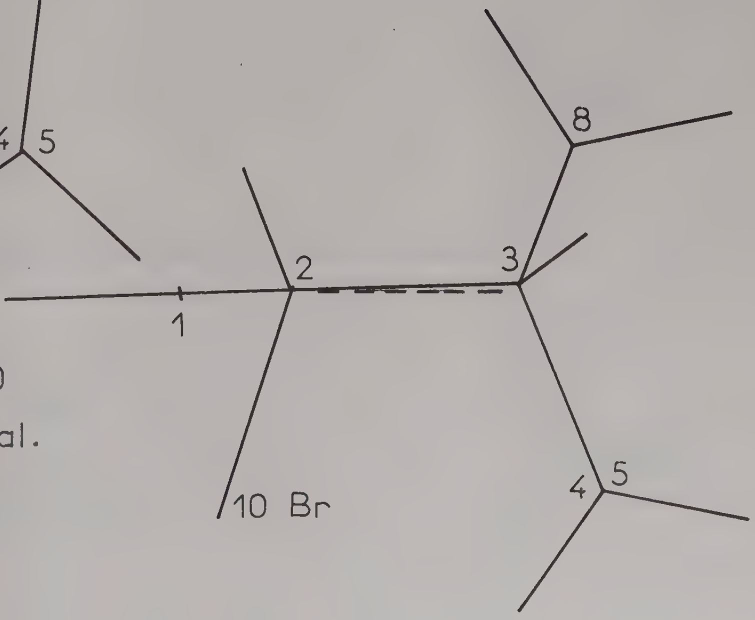


Figure 210
32,851 kcal.

bicyclo [3.2.1] octanone-3
α α' cis-dibromée

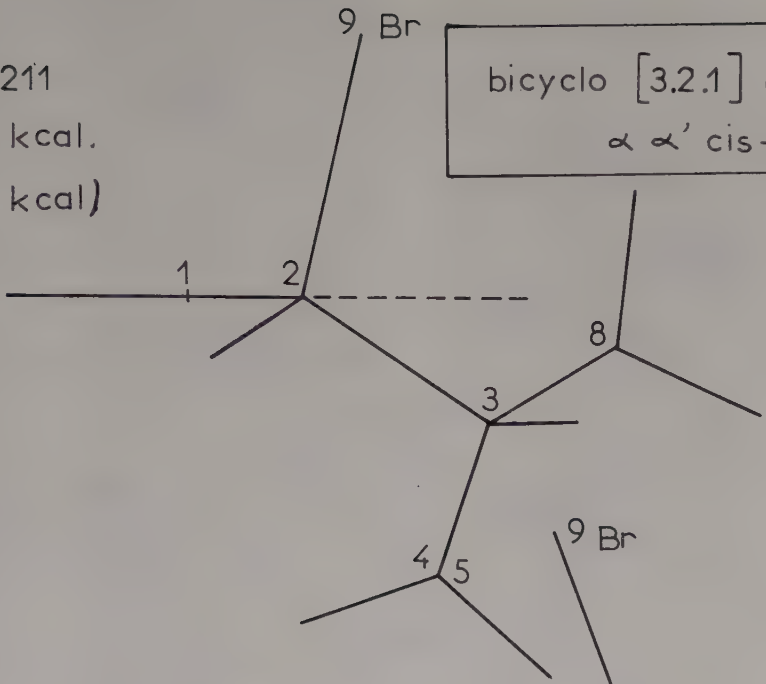


Figure 211
28,286 kcal.
(25,885 kcal)

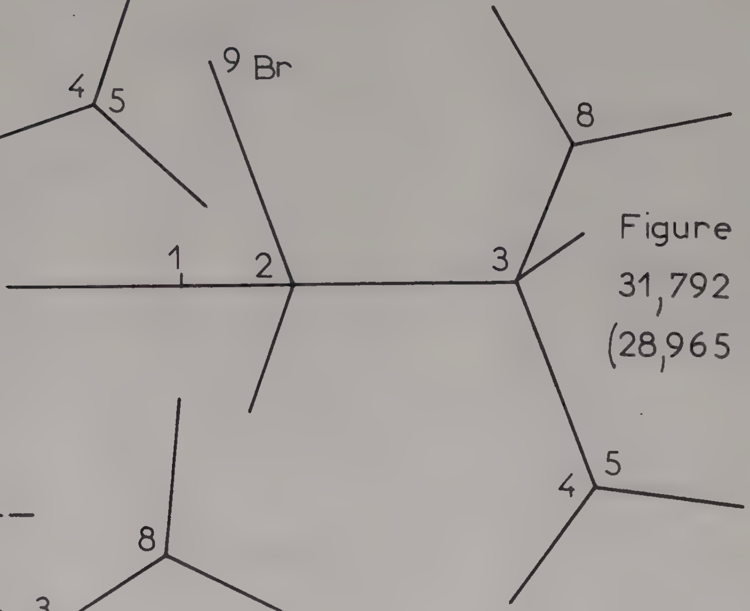


Figure 212
31,792 kcal.
(28,965 kcal)

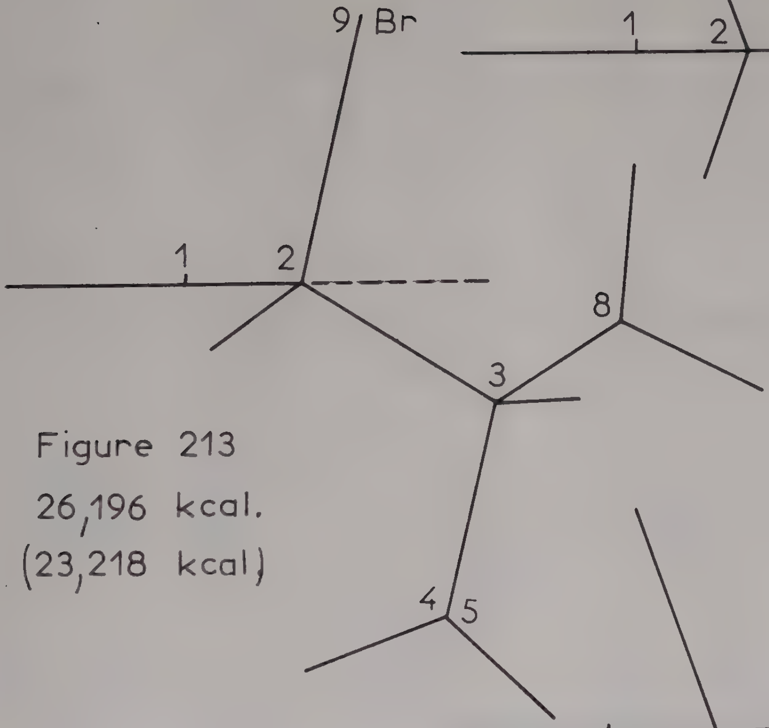


Figure 213
26,196 kcal.
(23,218 kcal)

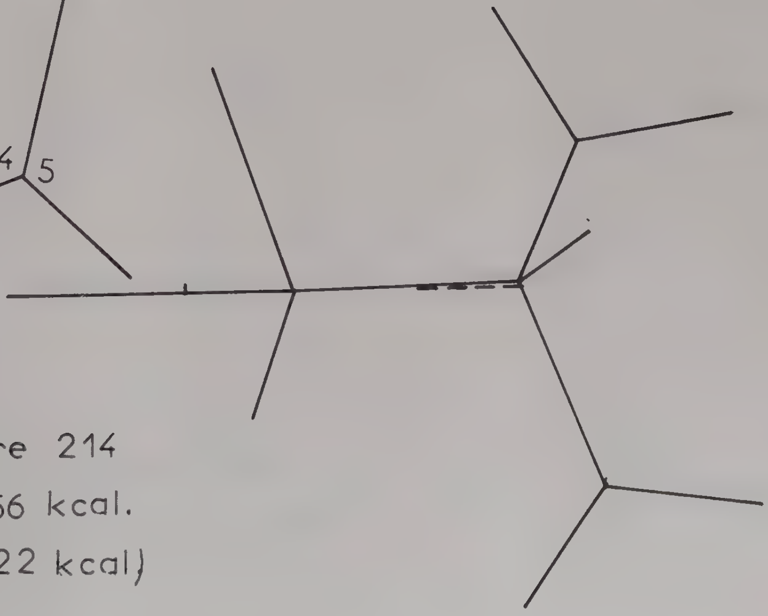


Figure 214
31,056 kcal.
(28,222 kcal)

bicyclo [3.2.1] octanone-3
αα' cis dibromée

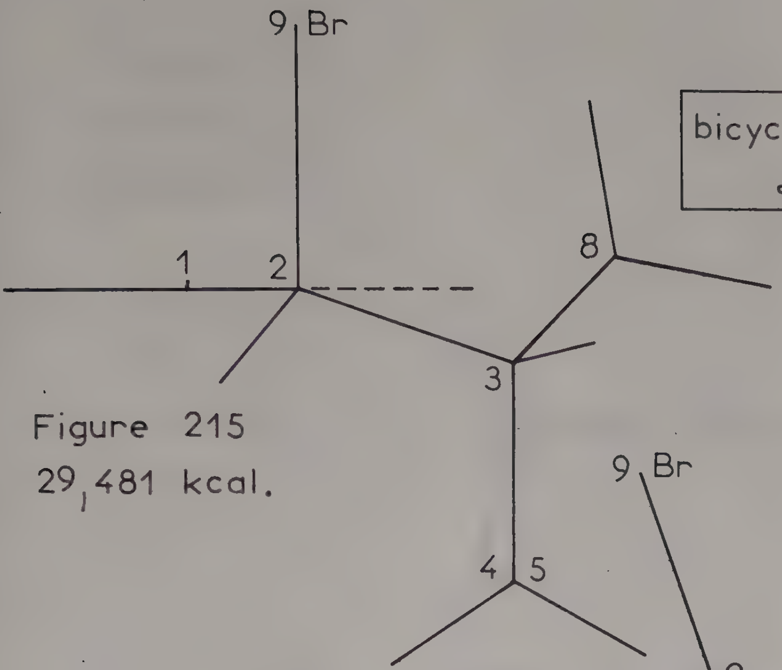


Figure 215
29,481 kcal.

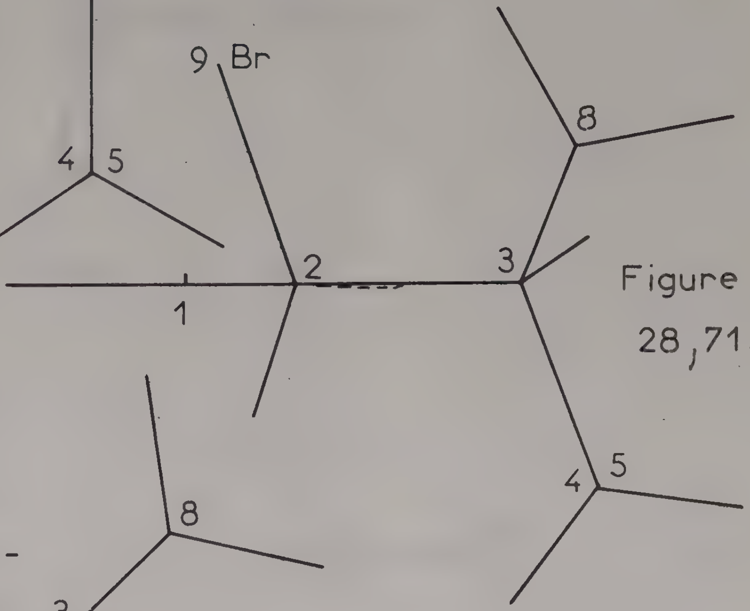


Figure 216
28,715 kcal.

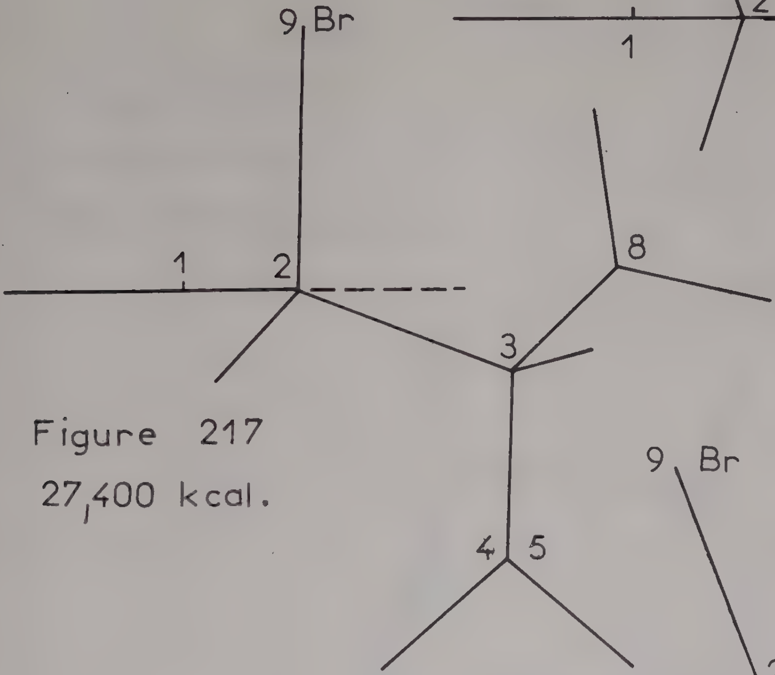


Figure 217
27,400 kcal.

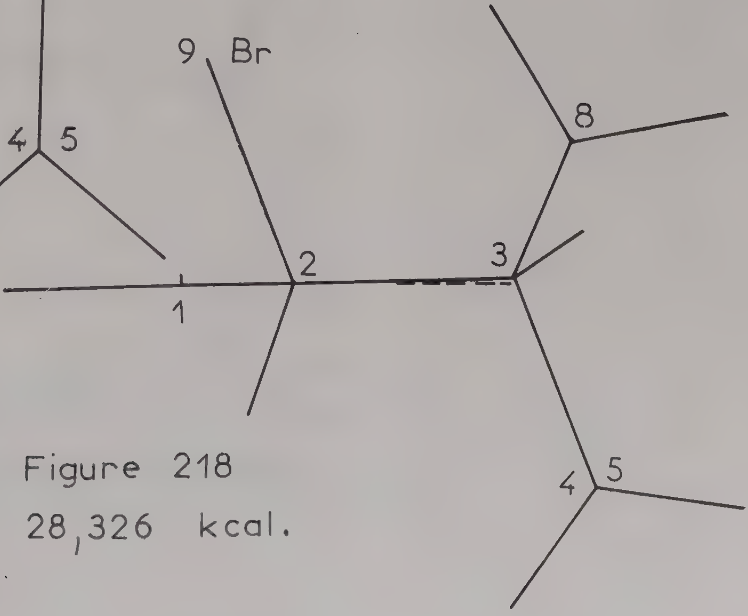


Figure 218
28,326 kcal.

Figure 219
31,603 kcal.
(28,086 kcal)

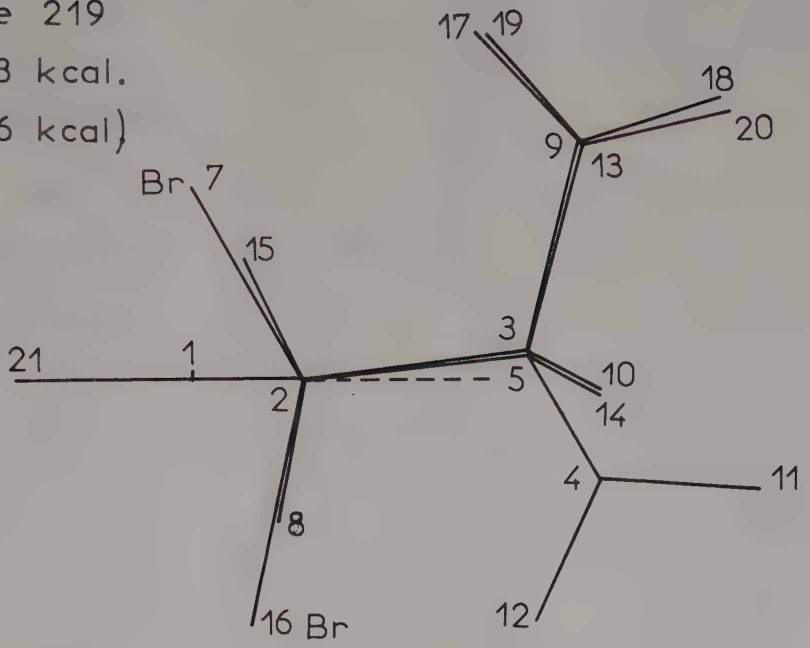
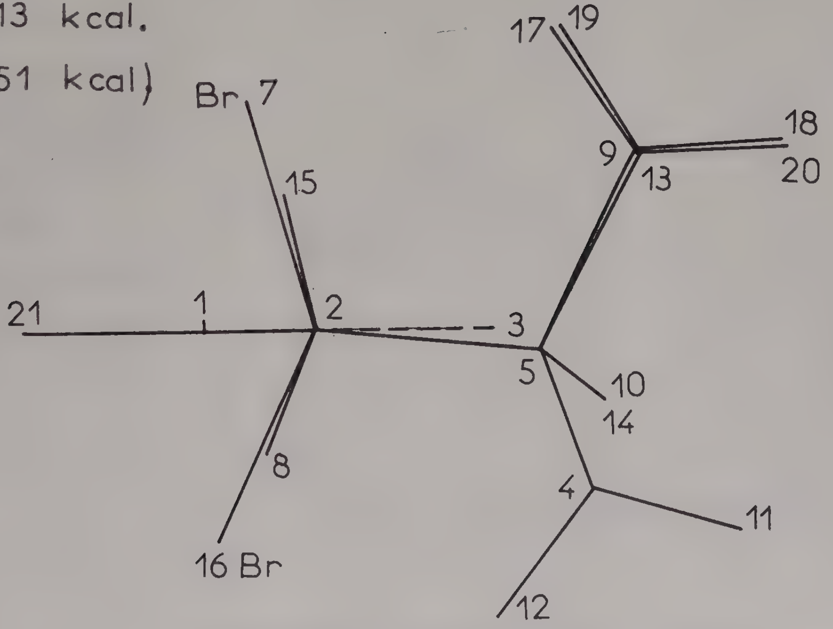


Figure 220
32,913 kcal.
(29,151 kcal)



bicyclo [3.2.1] octanone-3
αα' trans-dibromée

bicyclo [3.2.1]octène-6, one-3 et dérivé αα' cis-diméthylé

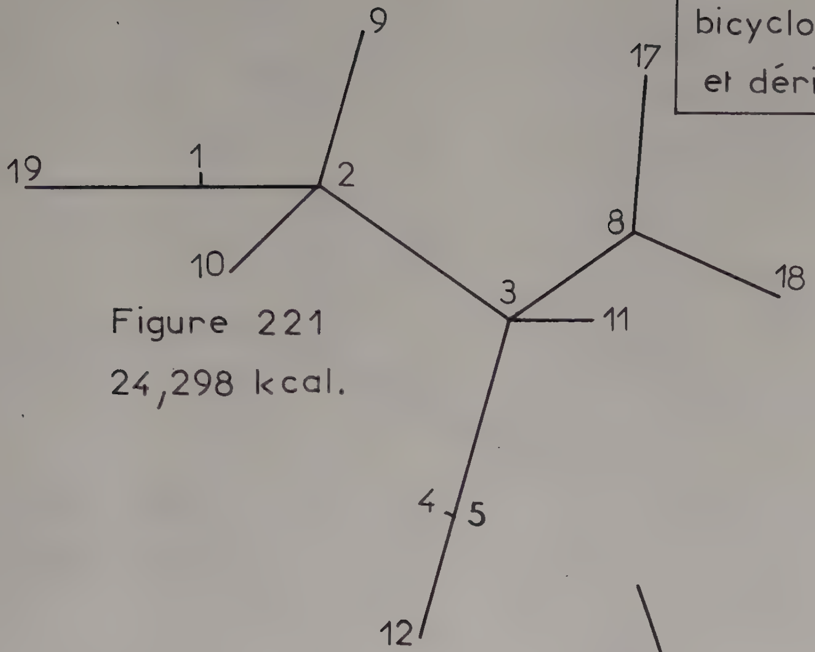


Figure 221
24,298 kcal.

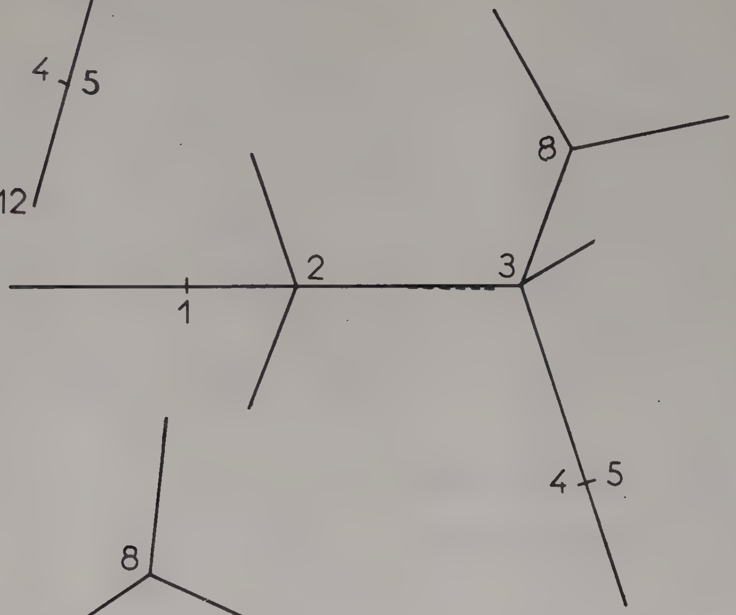


Figure 222
27,308 kcal.

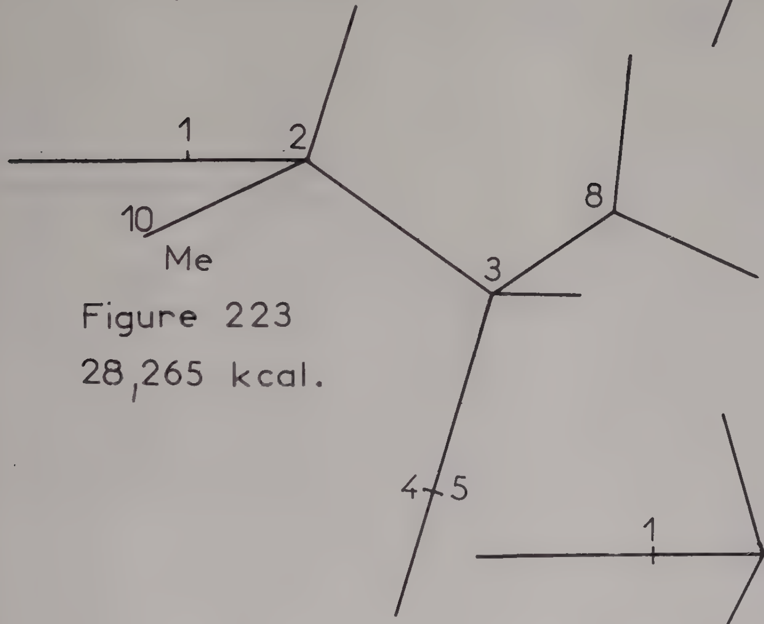


Figure 223
28,265 kcal.

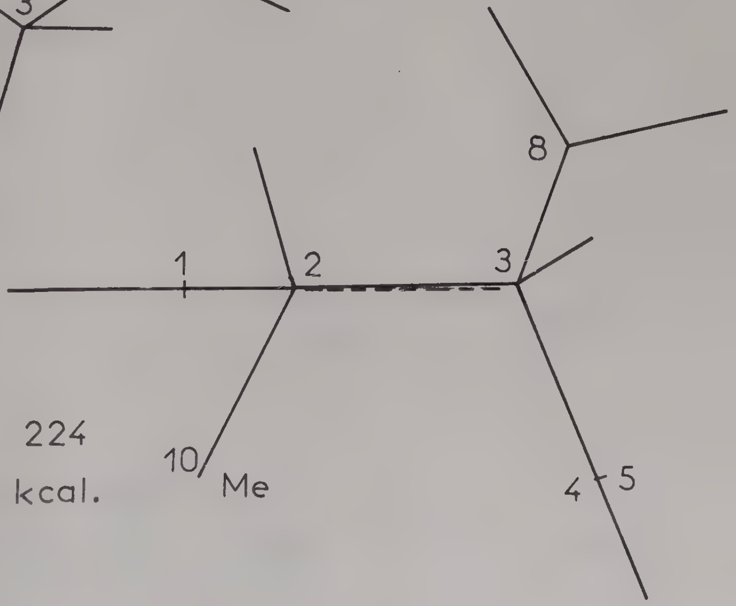


Figure 224
33,393 kcal.

bicyclo [3.2.1] octène-6, one-3
αα' cis-diméthylée et
αα α'α' tétraméthylée

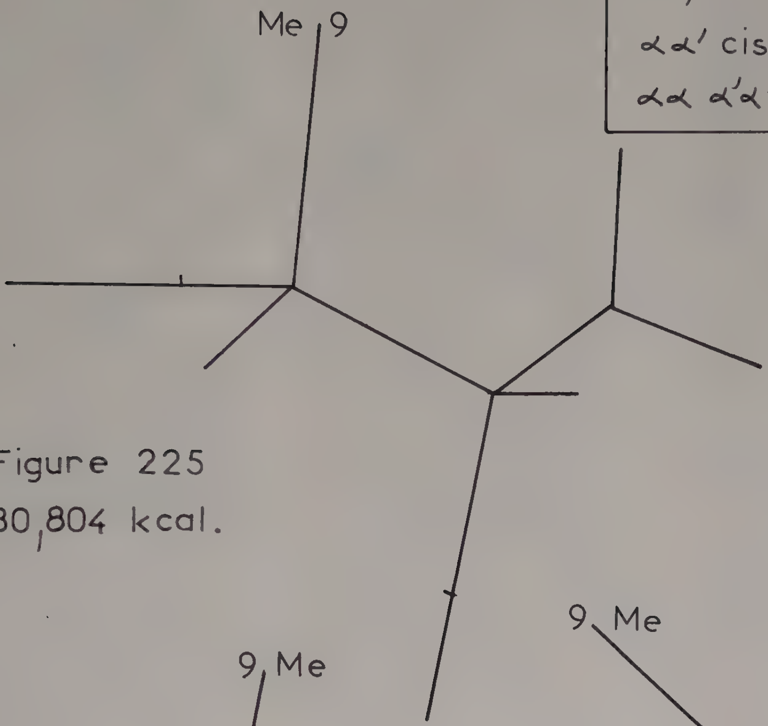


Figure 225
30,804 kcal.

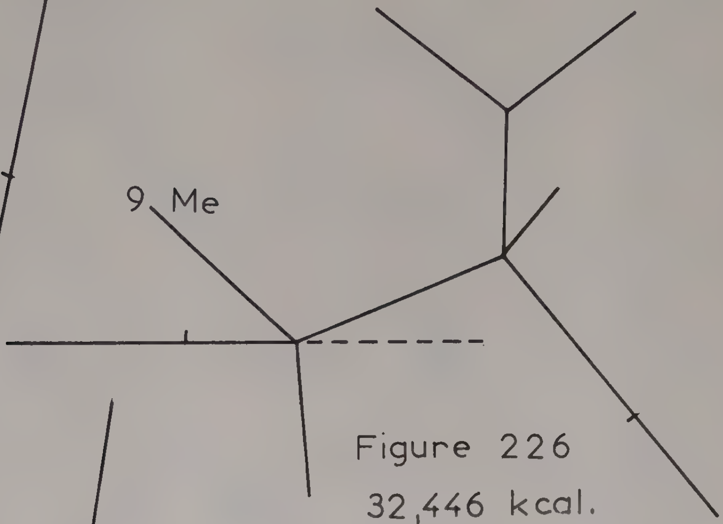


Figure 226
32,446 kcal.

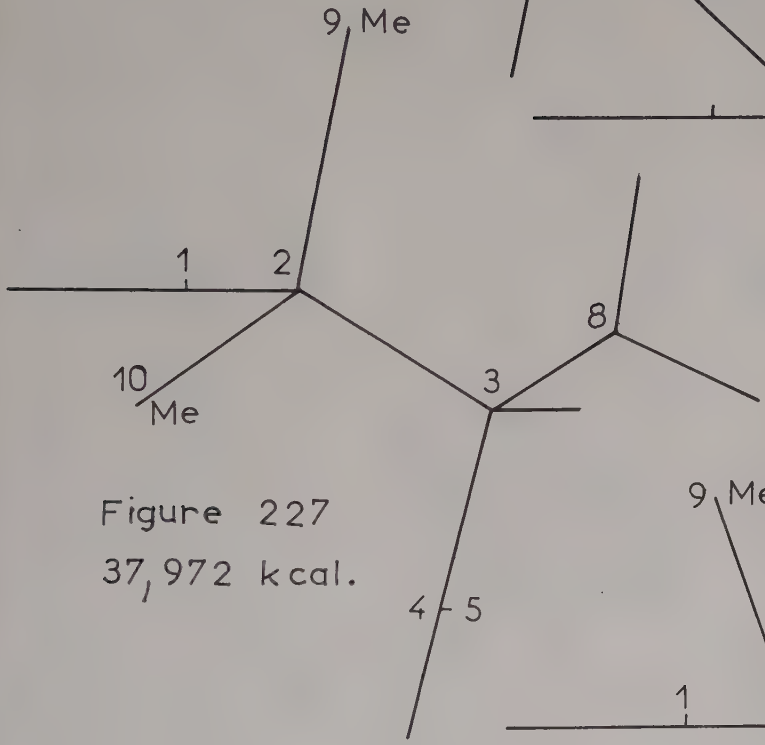


Figure 227
37,972 kcal.

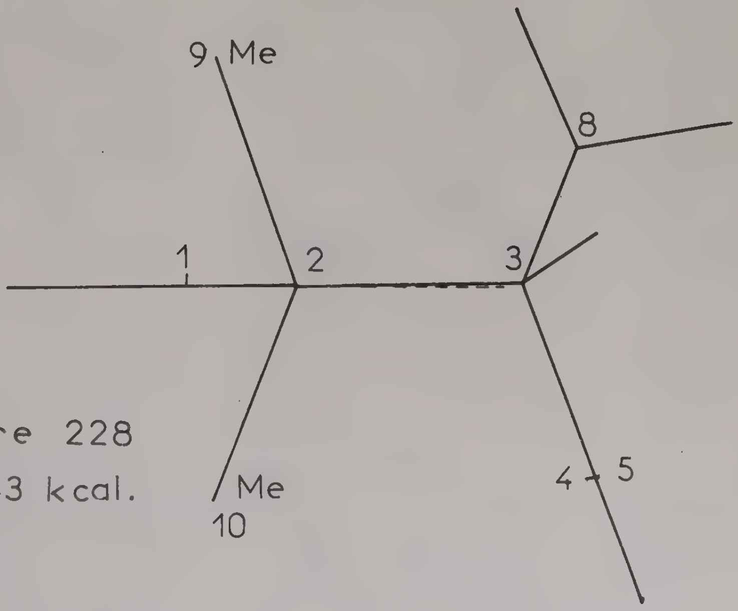


Figure 228
41,343 kcal.

bicyclo [3.2.1] octanol - 3

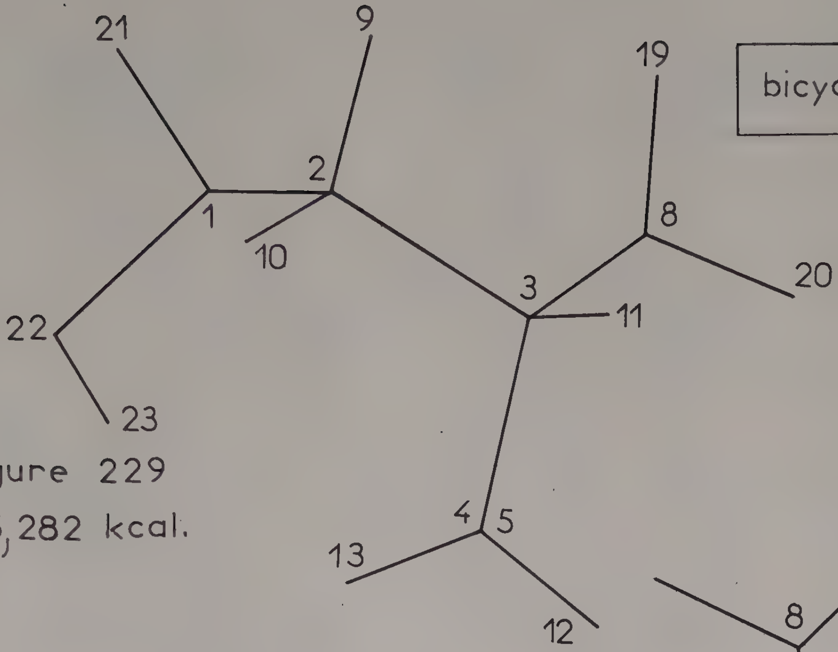


Figure 229
25,282 kcal.

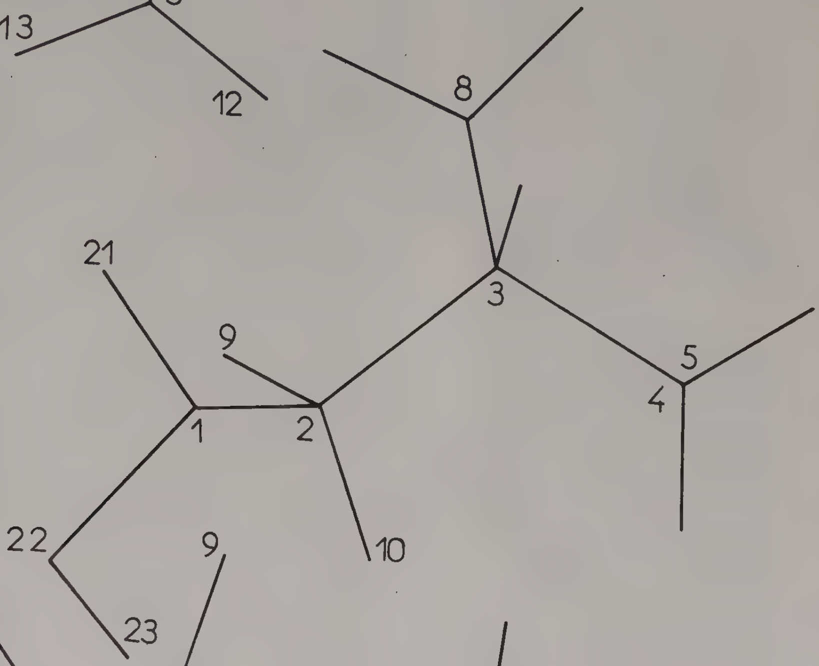


Figure 230
27,049 kcal.

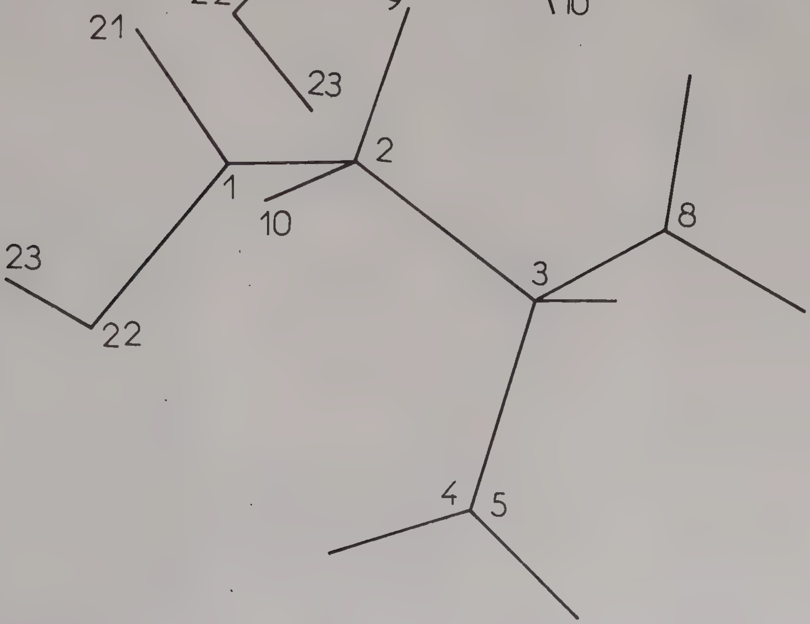


Figure 231
21,755 kcal.

bicyclo [3.2.1] octanol-3

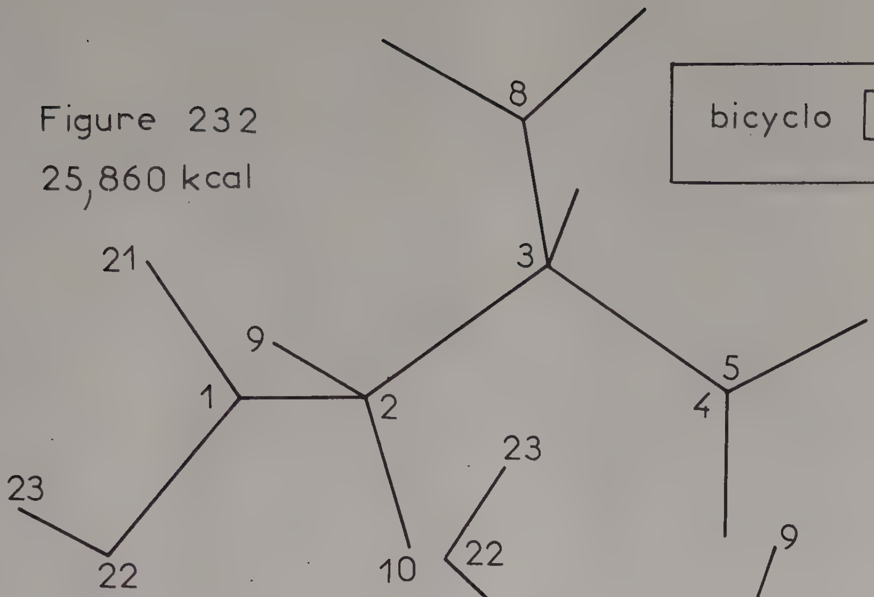


Figure 232
25,860 kcal

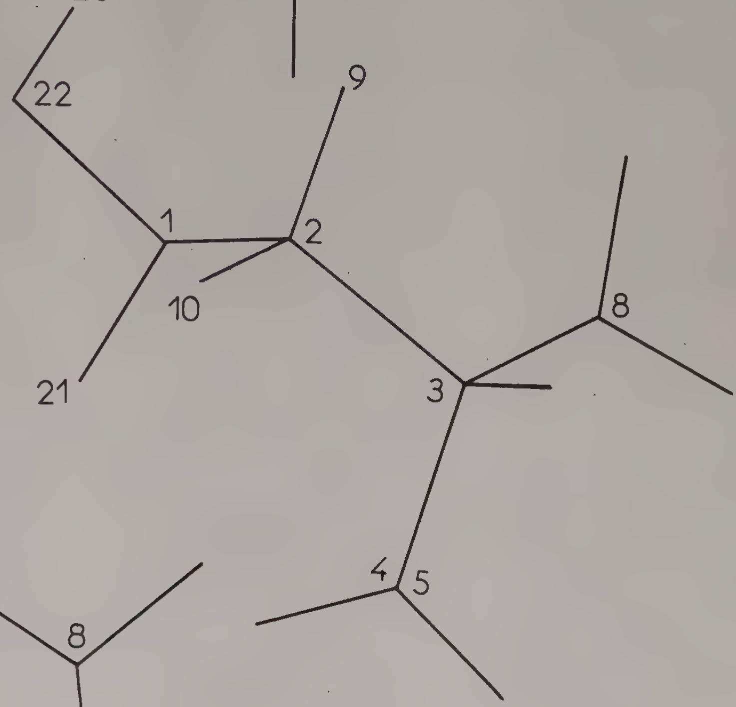


Figure 233
22,497 kcal.

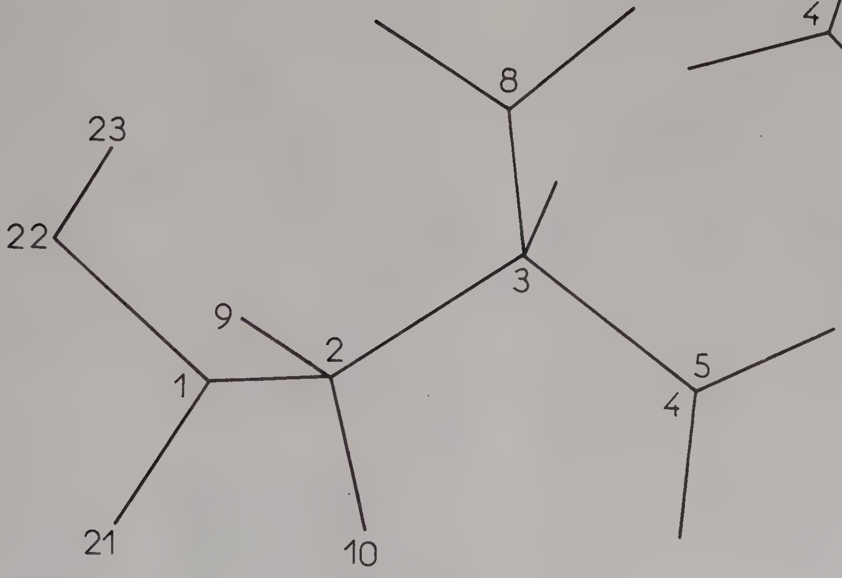


Figure 234
22,497 kcal.

bicyclo [3.2.1] octanol -3

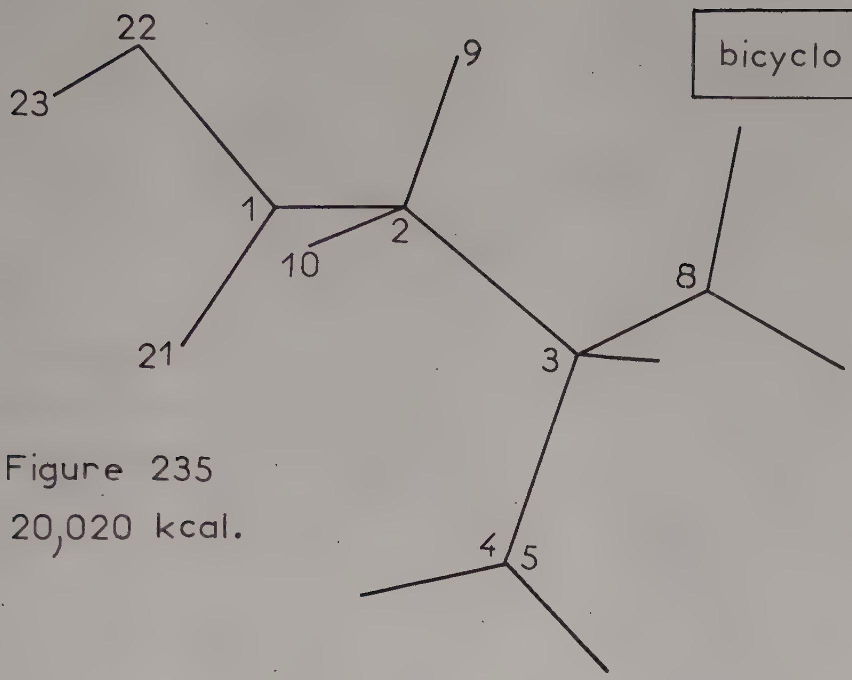


Figure 235
20,020 kcal.

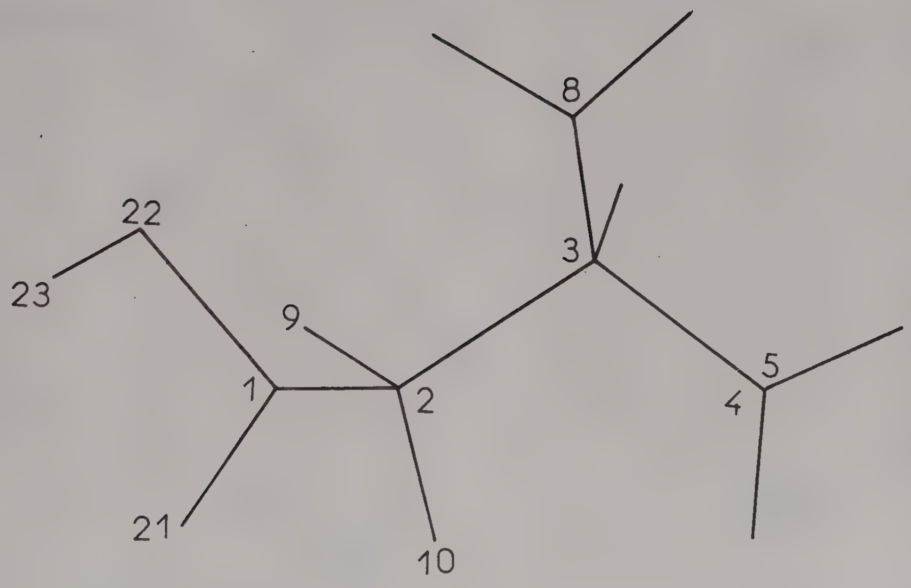


Figure 236
27,282 kcal.

méthyl-3 bicyclo [3.2.1] octanol-3

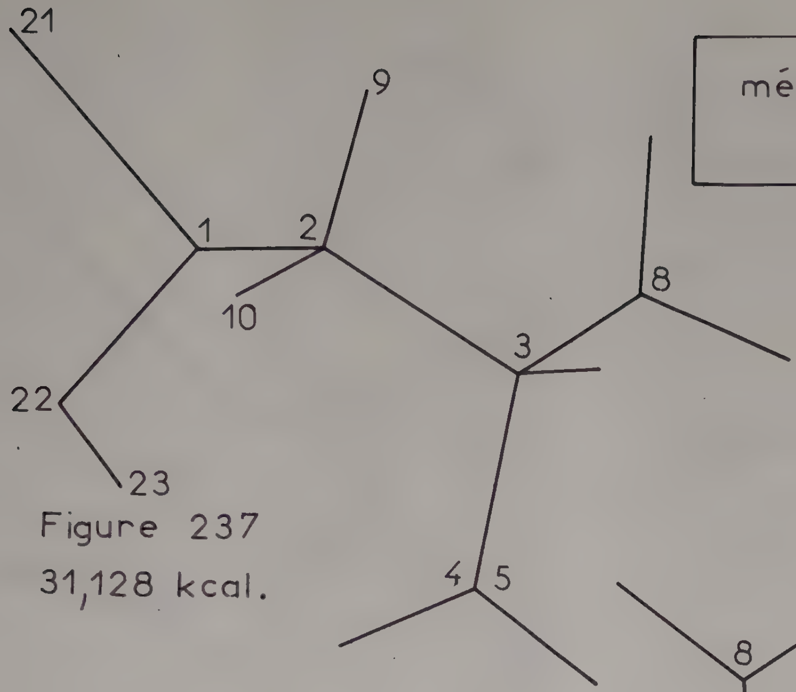


Figure 237
31,128 kcal.

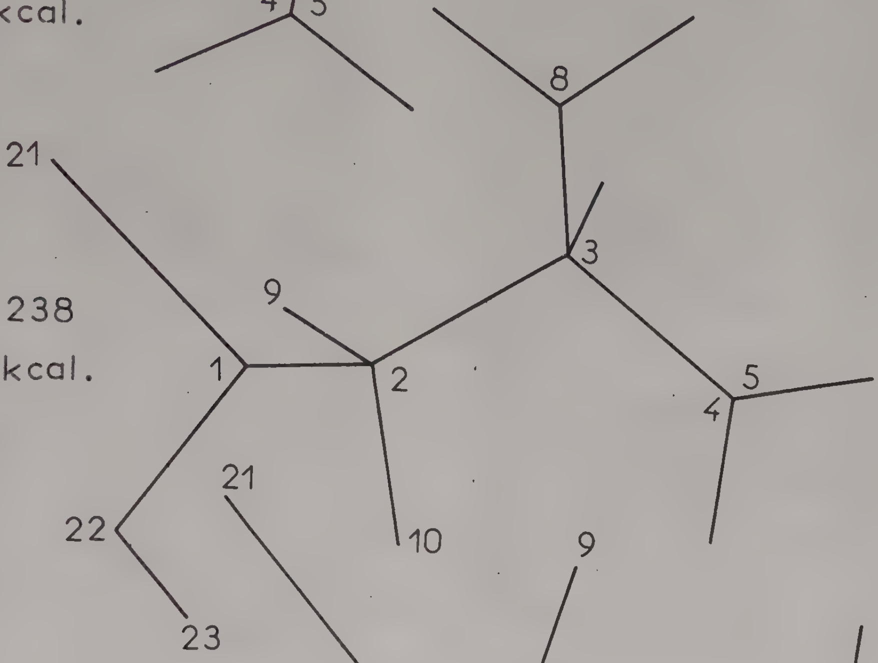


Figure 238
37,535 kcal.

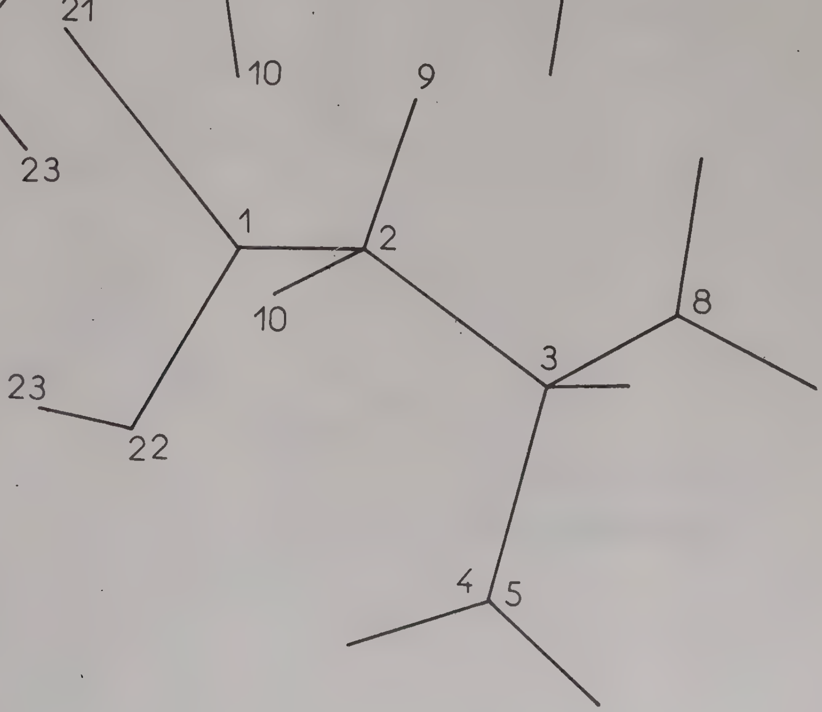


Figure 239
29,513 kcal.

méthyl-3 bicyclo [3.2.1] octanol-3

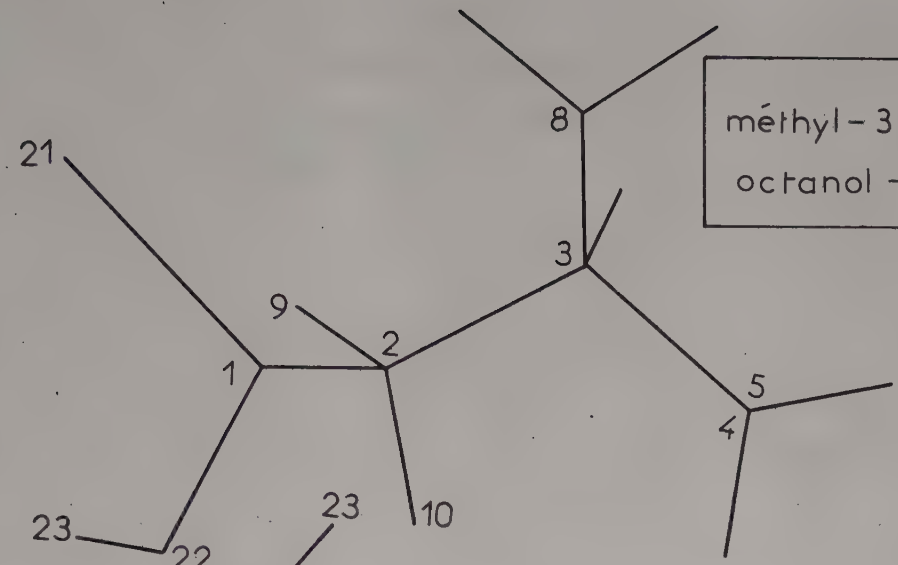


Figure 240
37,708 kcal.

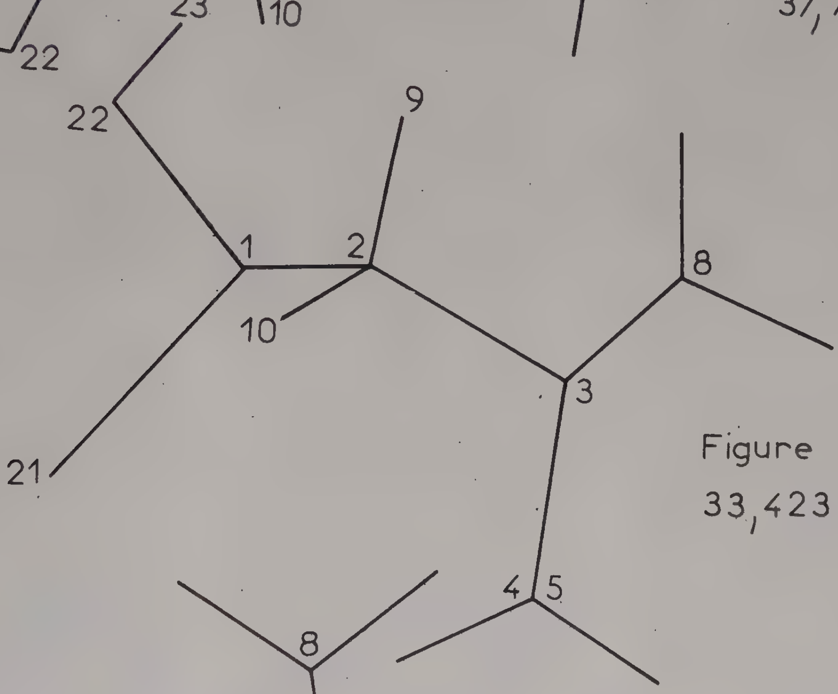


Figure 241
33,423 kcal.

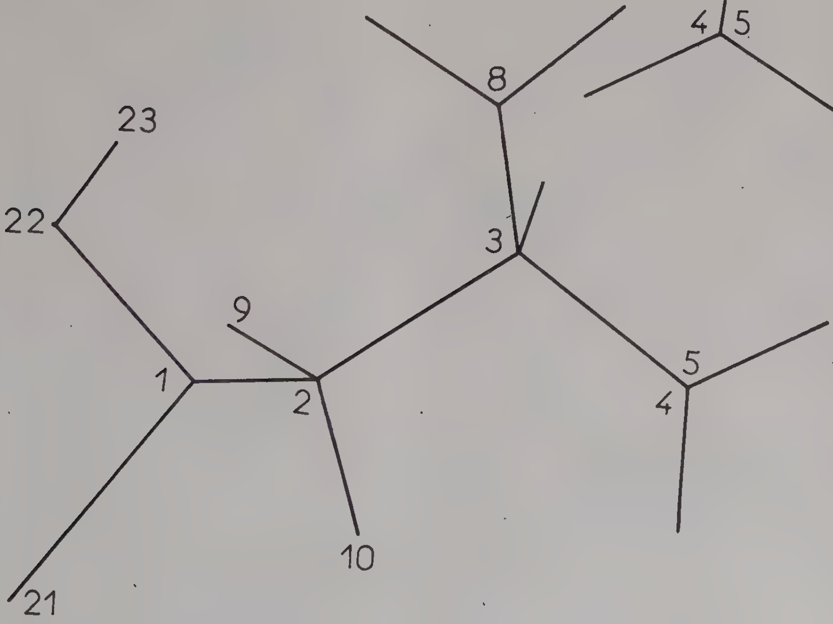


Figure 242
35,570 kcal.

méthyl-3 bicyclo [3 2 1] octanol-3

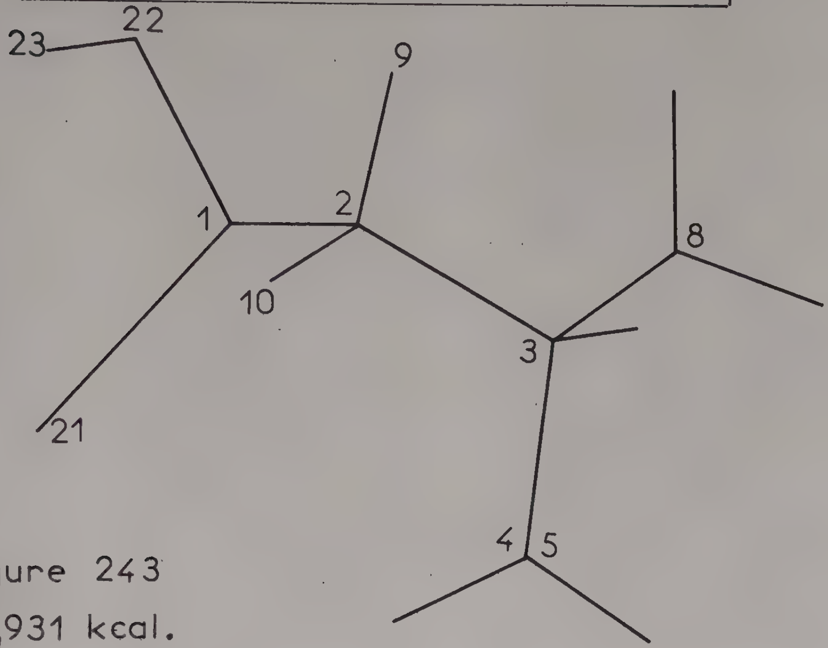


Figure 243
32,931 kcal.

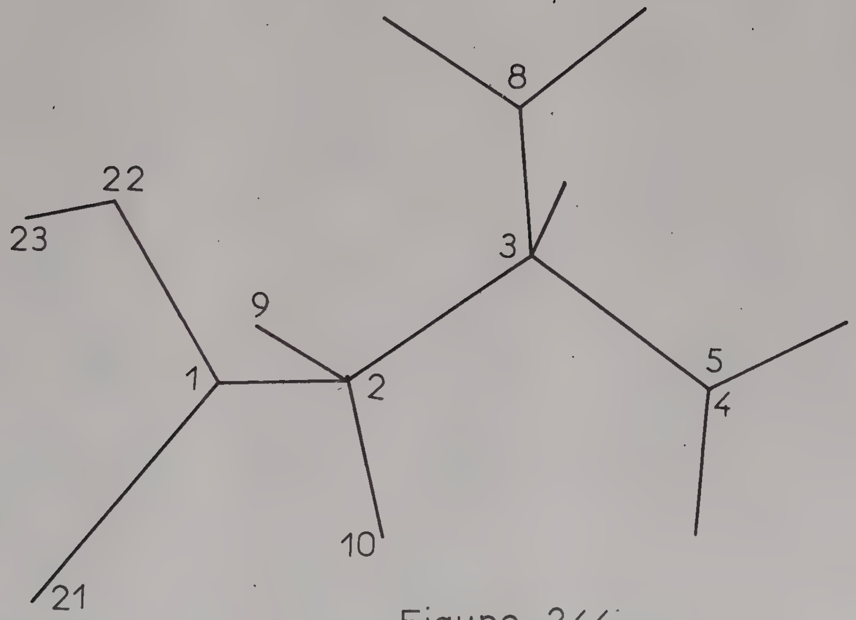


Figure 244
34,955 kcal.

bicyclo [3.2.1] octène-6,
ol-3

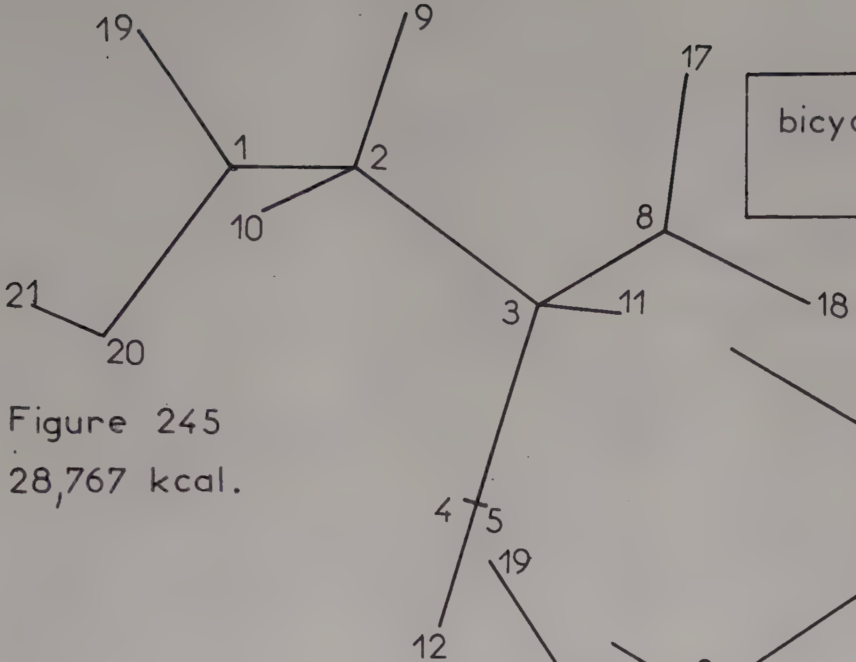


Figure 245
28,767 kcal.

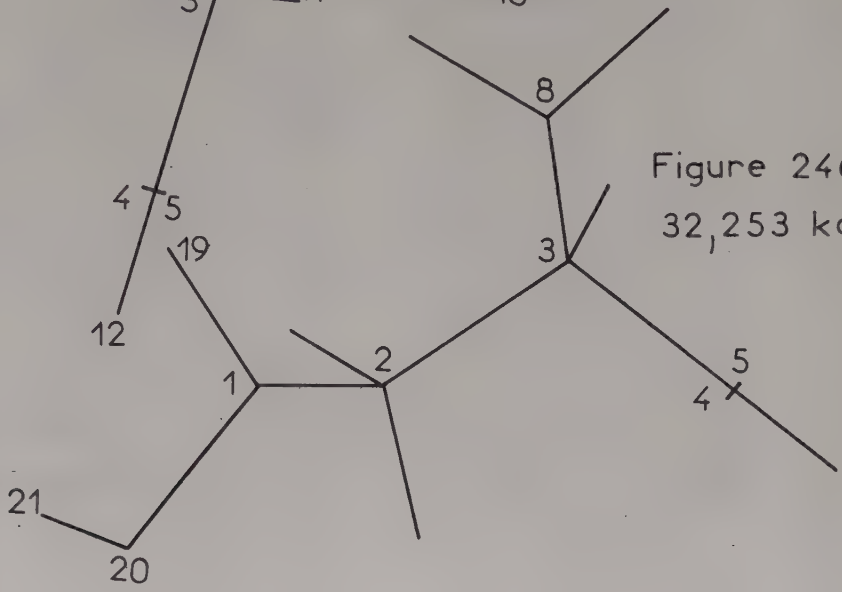


Figure 246
32,253 kcal.

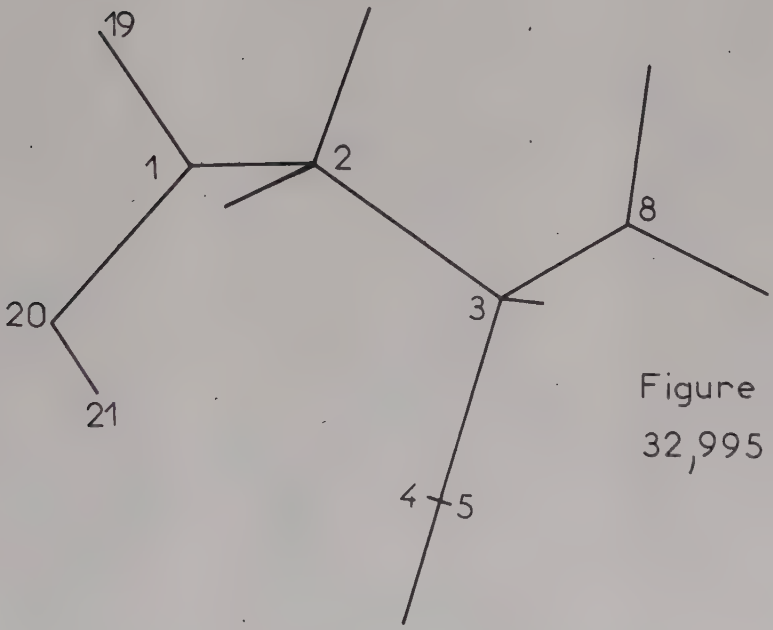


Figure 247
32,995 kcal.

bicyclo [3.2.1] octène-6, ol-3

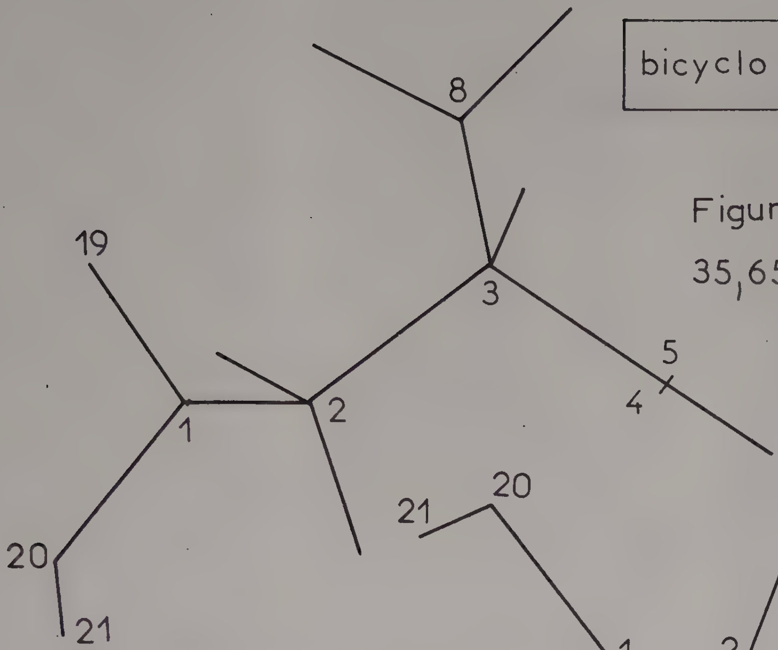


Figure 248
35,653 kcal.

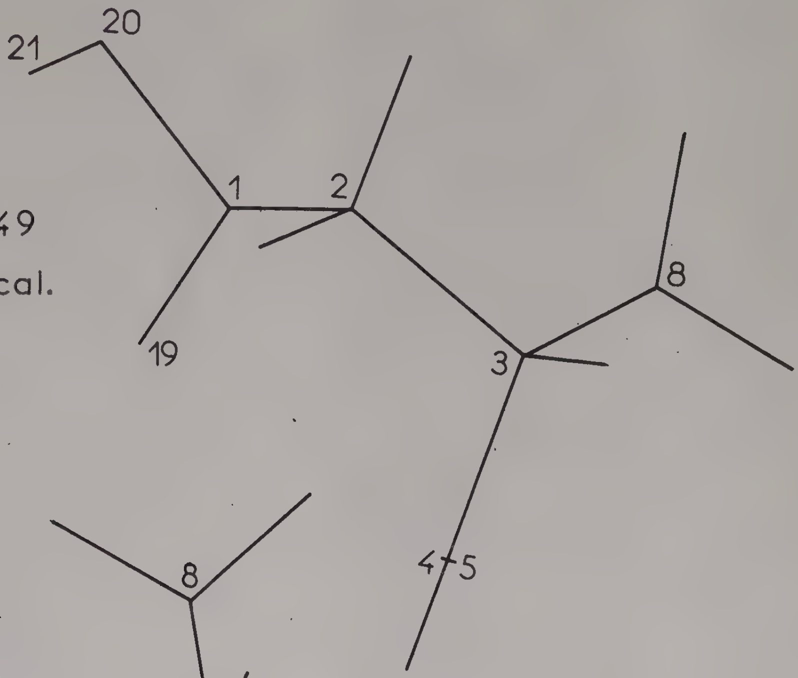


Figure 249
27,252 kcal.

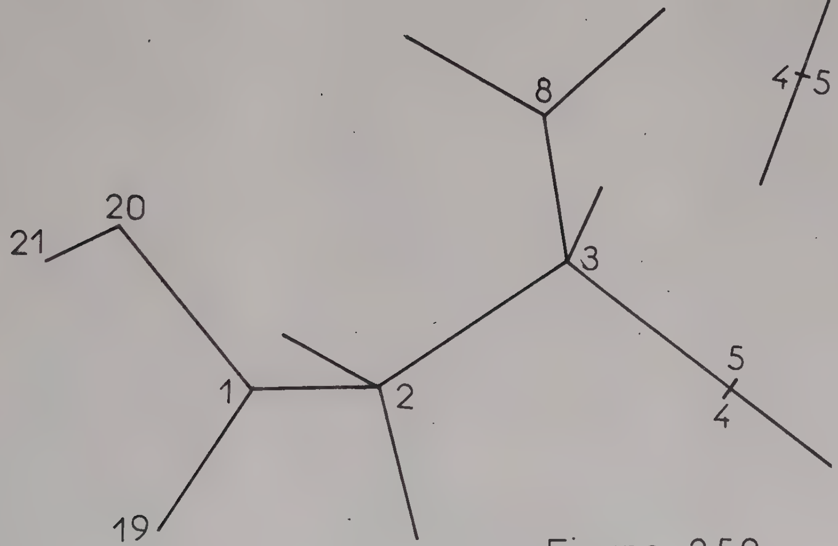


Figure 250
33,639 kcal.

bicyclo [3.2.1] octène-6, ol-3

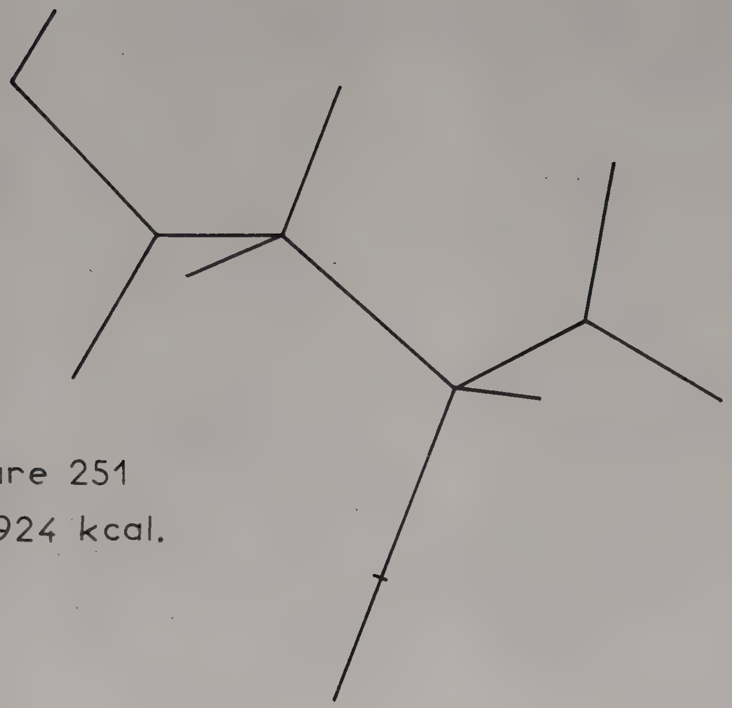


Figure 251
30,924 kcal.

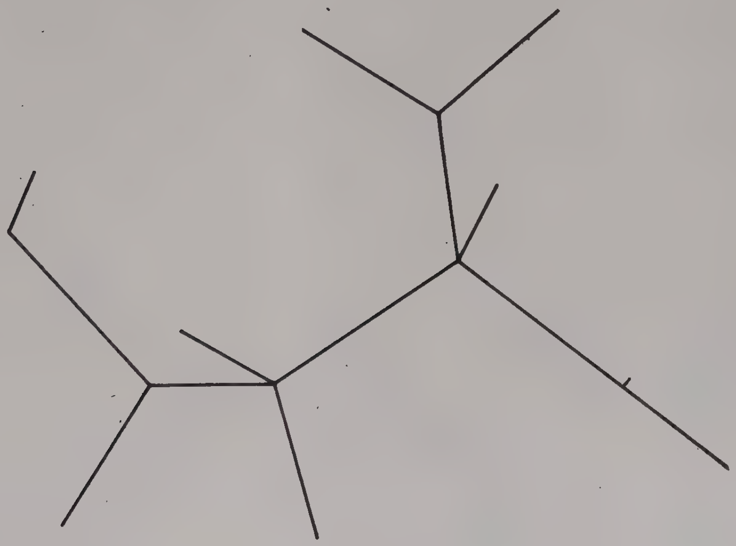
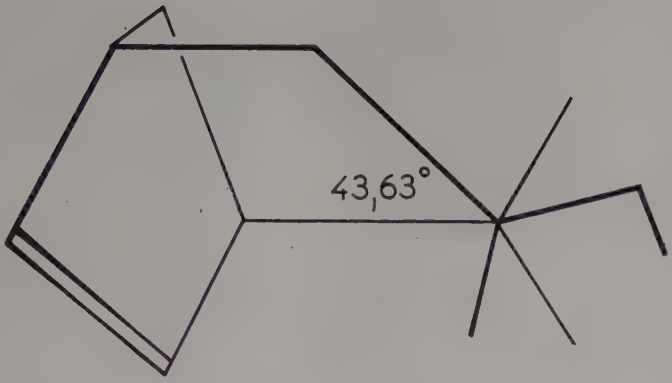
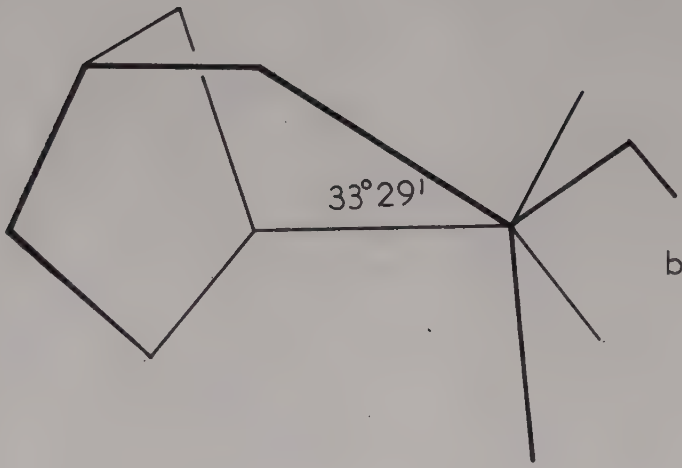


Figure 252
37,950 kcal.

Figure 253

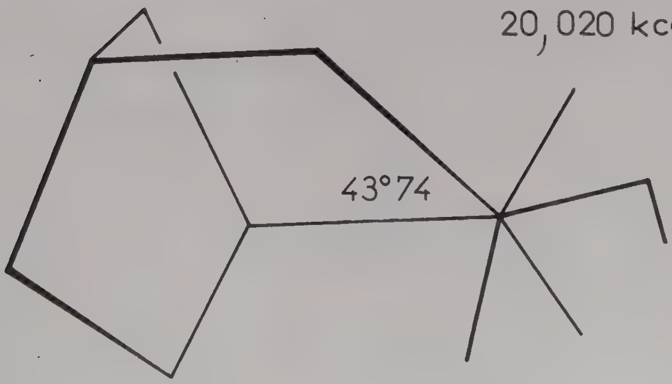


bicyclo [3-2-1] octène 6, ol-3
27,252 kcal.



méthyl-3
bicyclo [3.2.1] octanol 3
32,931 kcal.

bicyclo [3.2.1] octanol-3
20,020 kcal.

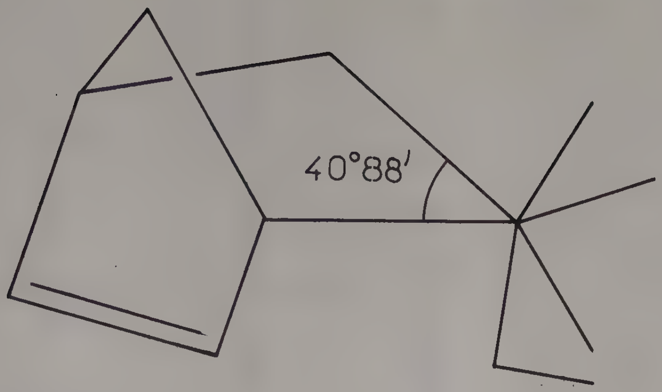


isomères exo.

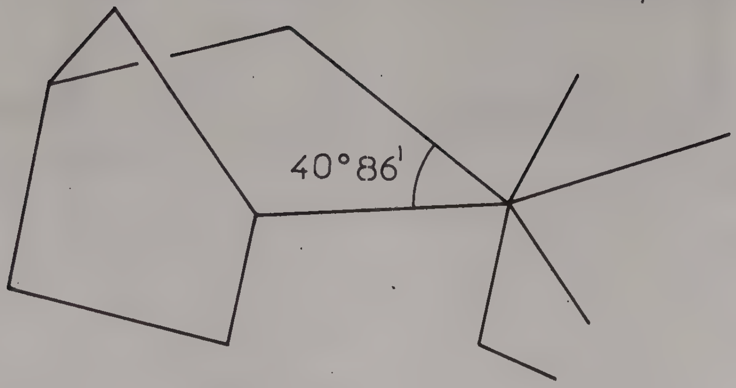
Figure 254

isomères endo

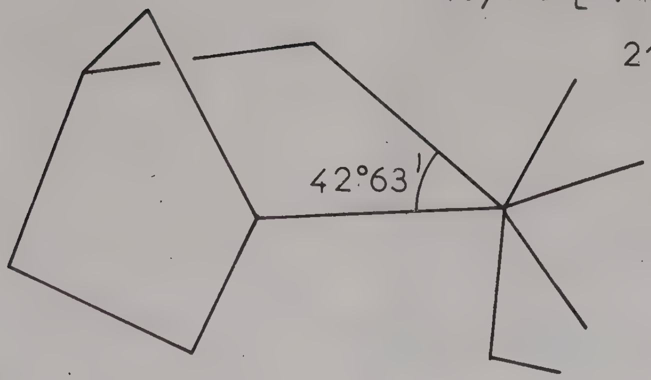
bicyclo [3.2.1] octene-6, ol-3
28,767 kcal.

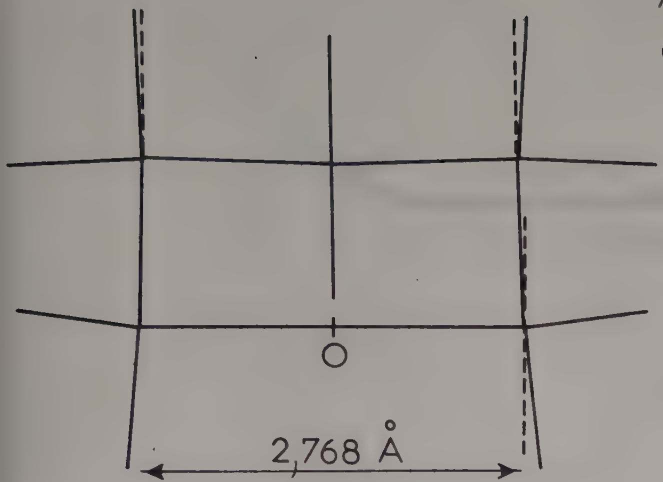


Méthyl-3 bicyclo [3.2.1] octanol-3
29,513 kcal.

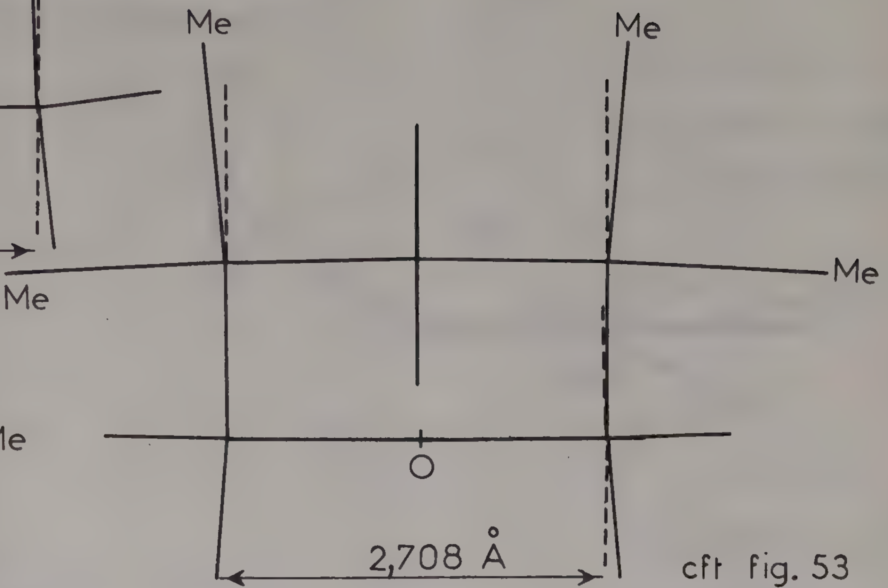


bicyclo [3.2.1] octanol-3
21,755 kcal.



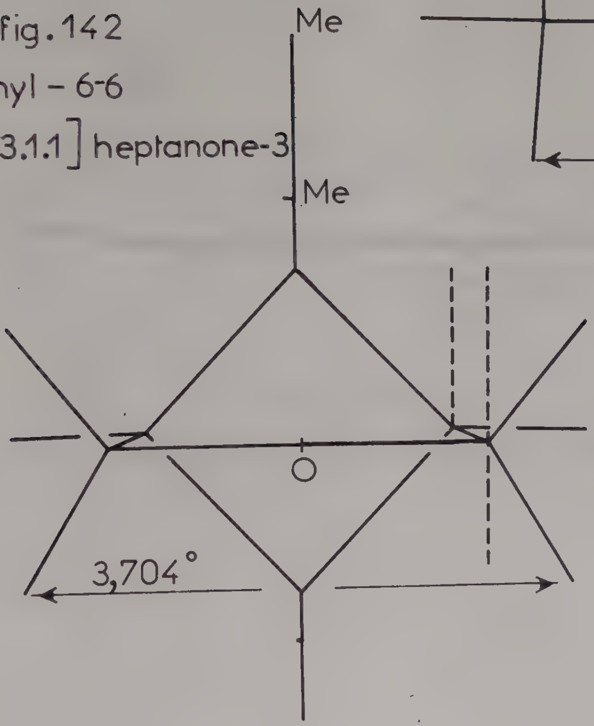


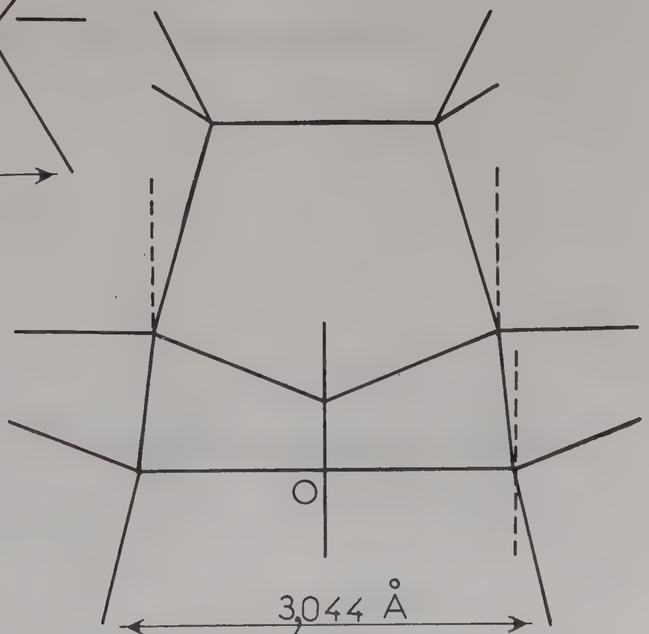
cyclohexanone
cft fig. 43



cft fig. 53
tétraméthyl -3,3,5,5
cyclohexanone

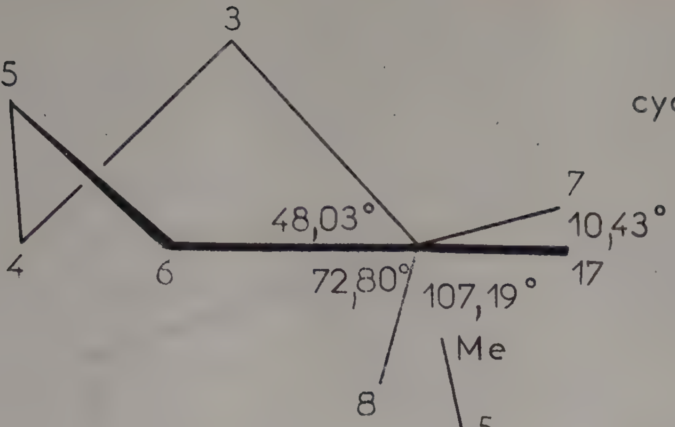
cft fig. 142
diméthyl - 6-6
bicyclo [3.1.1] heptanone-3



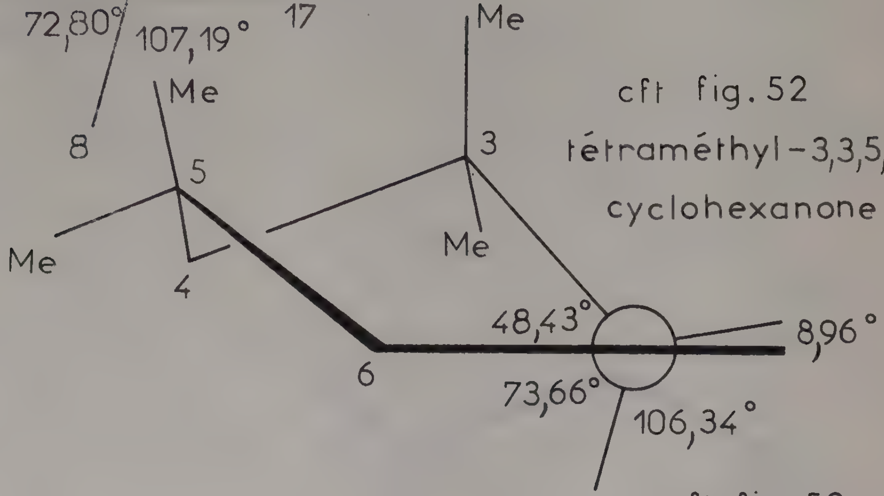


bicyclo [3.2.1] octanone-3 cft fig.187

Figure 255 - cétones
projections dans le plan x z
(programmes à symétrie
imposée)

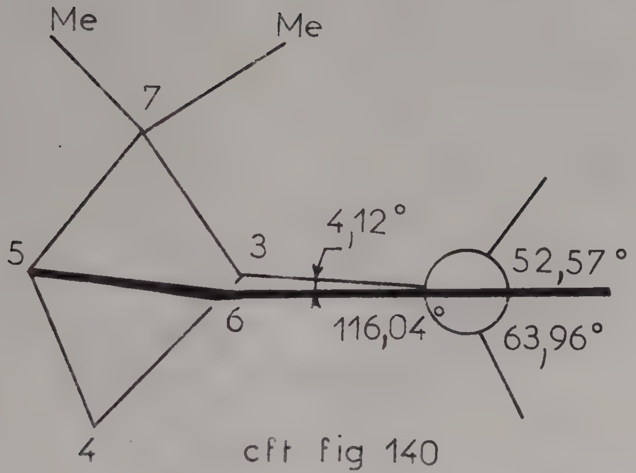


cft fig.41
cyclohexanone

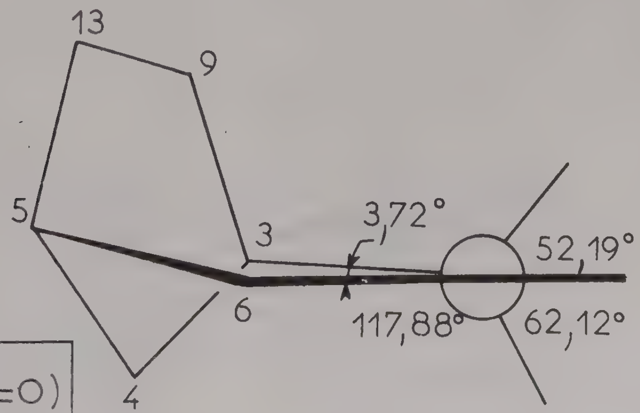


cft fig.52
tétraméthyl-3,3,5,5
cyclohexanone

cft fig.52
tétraméthyl-3,3,5,5
cyclohexanone

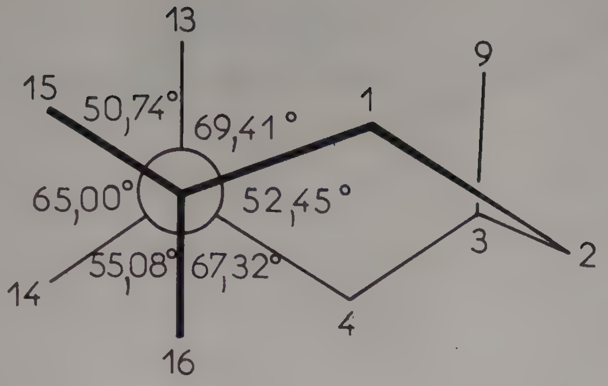


cft fig 140
diméthyl-6,6 bicyclo [3.1.1] heptanone-3

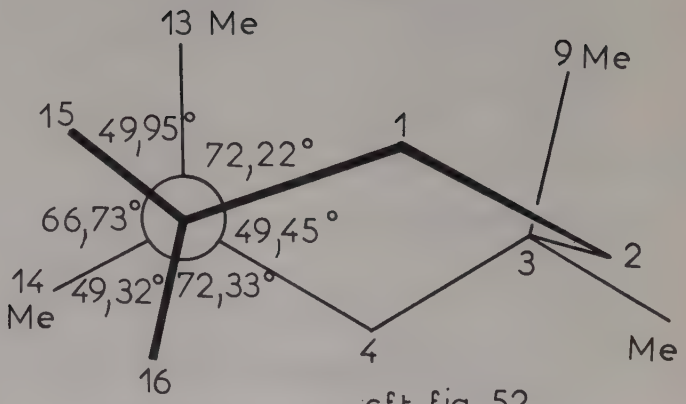


cft fig.183
bicyclo [3.2.1] octanone-3

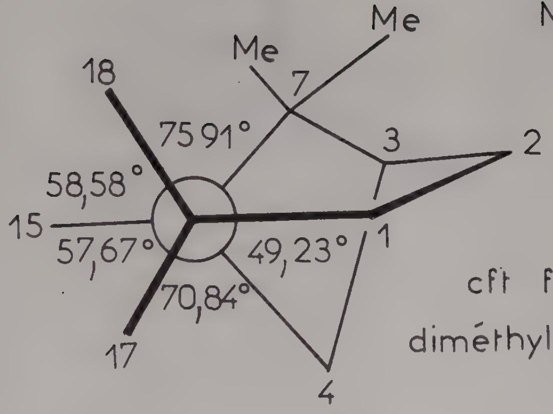
Figure 256 cétones
projections de Newman
des angles dièdres dont
l'arête est la liaison C–C(=O)
(programmes sans symétrie
imposée)



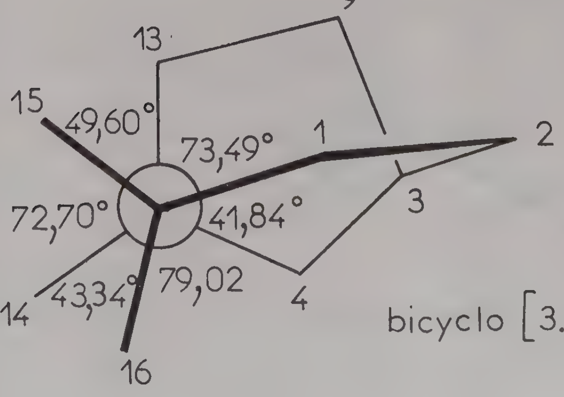
cft fig. 41
cyclohexanone



cft fig. 52
tétraméthyl- 3,3,5,5
cyclohexanone

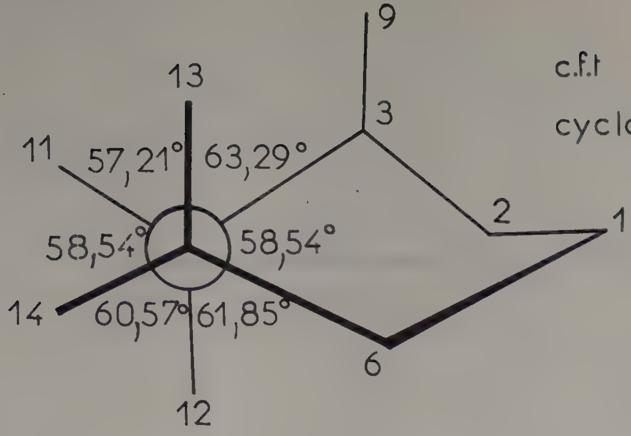


cft fig. 140
diméthyl-6,6 bicyclo [3.1.1] heptanone-3

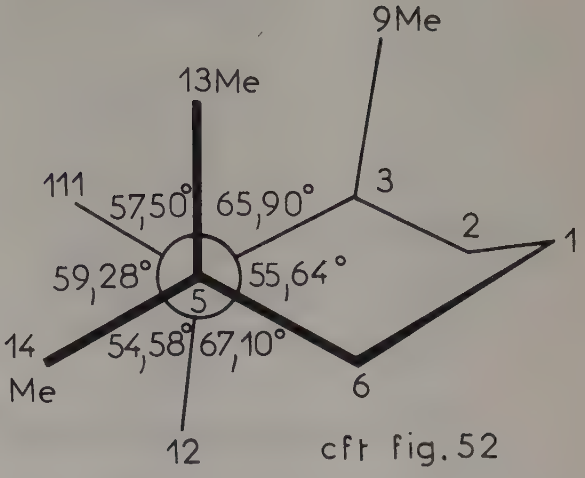


bicyclo [3.2.1] octanone-3

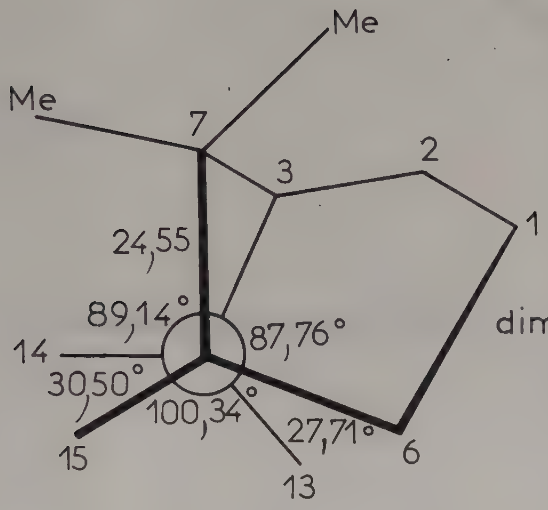
Figure 257- cétones
projections de Newman
des dièdres dont l'arête
est la liaison $C_\beta - C_\alpha$ par
par rapport au carbonyle



c.f.t fig. 41
cyclohexanone

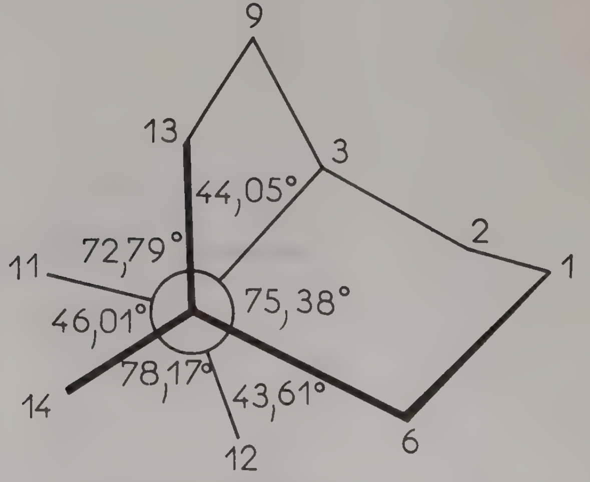


cft fig. 52
tétraméthyl-3,3,5,5
cyclohexanone



cft fig 140
diméthyl-6,6 bicyclo [3.1.1]
heptanone - 3

fig 258 cétones
projections de
Newman des dièdres
d'arête $C_\beta - C_\gamma$



cft fig. 183
bicyclo [3.2.1] octanone

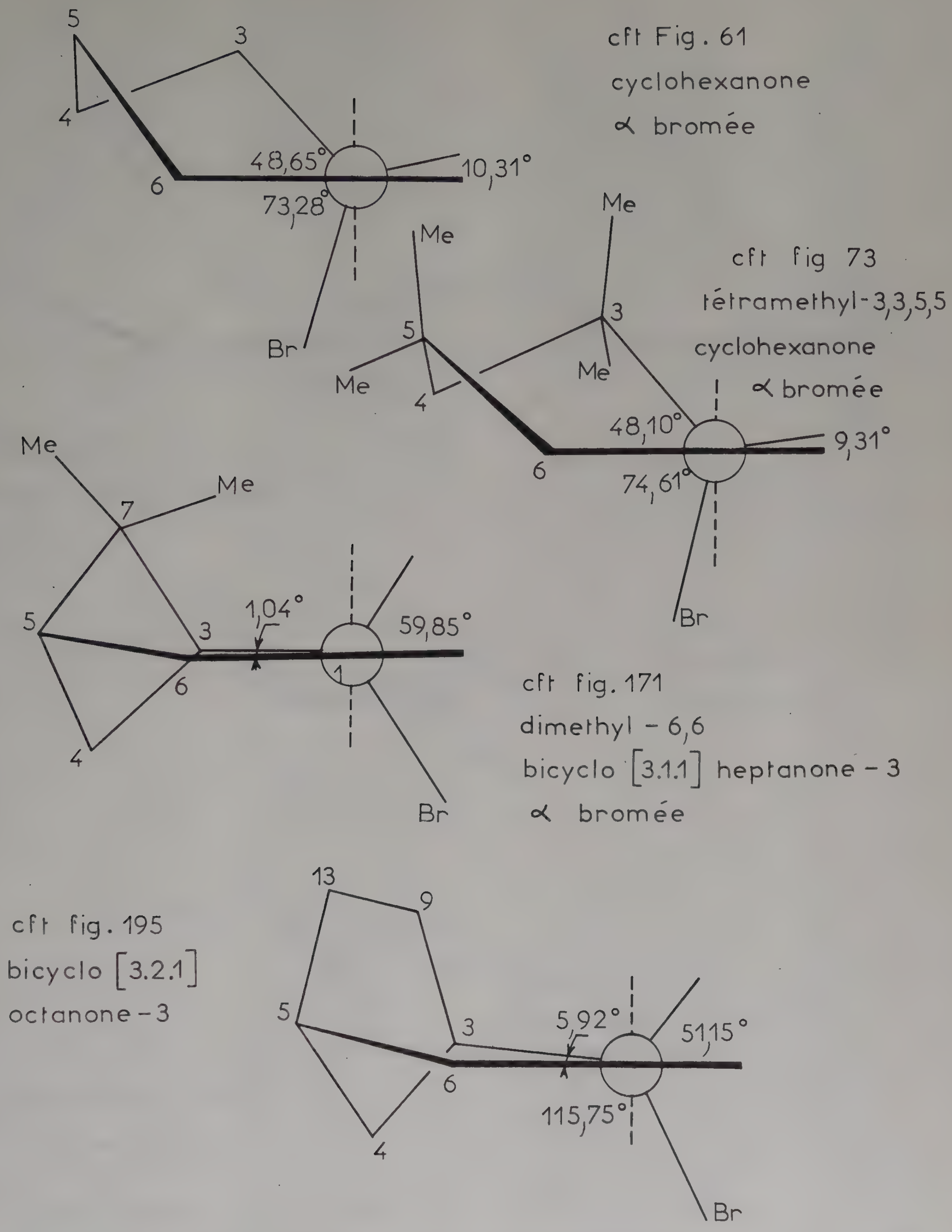
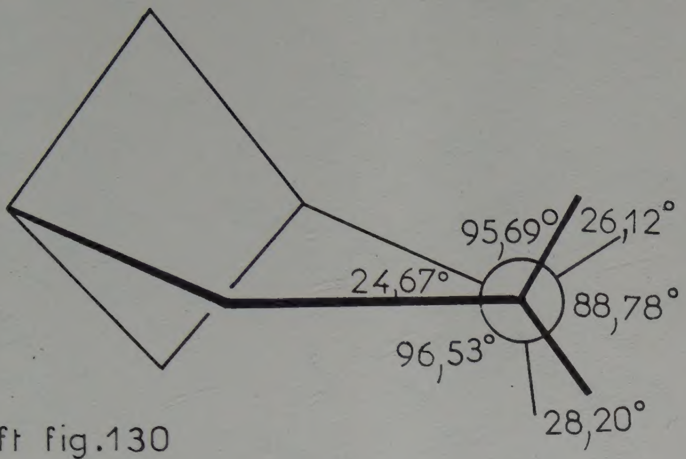
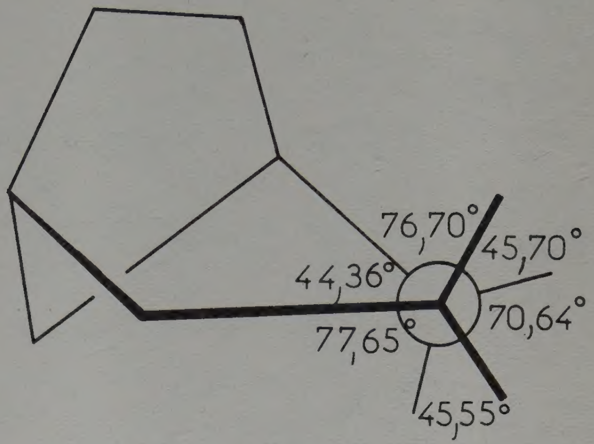


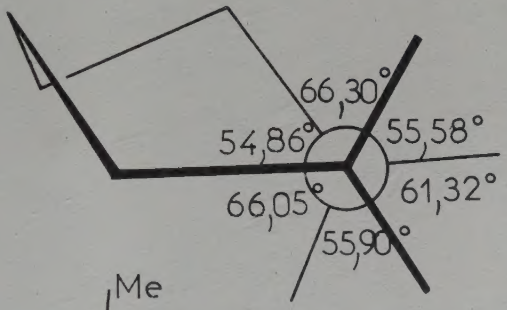
fig. 259 α - bromo cétones - projections de Newman des dièdres d'arête C — C(=O)



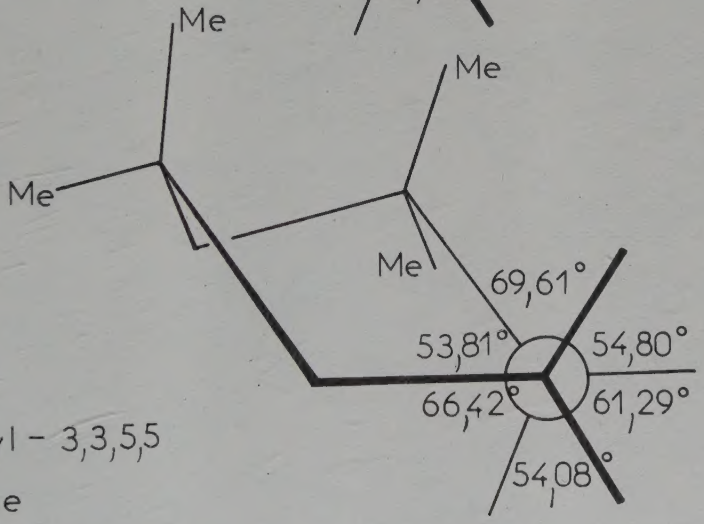
cft fig.130
bicyclo [3.1.1] heptane



cft fig.181
bicyclo [3.2.1] octane



cft. fig.5
cyclohexane



cft. fig.33
tétraméthyl - 3,3,5,5
cyclohexane

fig.260 : hydrocarbures projections de Newman
(programmes à symétrie imposée)